

A  
COMPARATIVE VIEW  
OF THE  
PHLOGISTIC AND ANTIPHLOGISTIC  
THEORIES.

*WITH INDUCTIONS.*

TO WHICH IS ANNEXED,  
AN  
ANALYSIS OF THE HUMAN CALCULUS,  
WITH OBSERVATIONS ON ITS ORIGIN, &c.

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BY WILLIAM HIGGINS,  
OF PEMBROKE COLLEGE, OXFORD.

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THE SECOND EDITION.

EST QUODAM PRODIRE TENUS, SI NON DATUR ULTRA.

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INTRODUC-



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## INTRODUCTION.

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ON comparing the present state of chemical knowledge with that which prevailed twelve years since, I trust that every true friend of philosophy will join me in contemplating with pleasure the rapid improvements which, even during that short period, have been made in this noble science. And, provided the present ardent spirit of inquiry continues to diffuse itself, it must shortly ripen chemistry into such perfection, as will contribute more to the

welfare and happiness of mankind in general, than can at present be imagined.

He who first made glass, or extracted a metal from its ore, knew not the value of his discovery ; nor did he foresee the benefits that would arise to mankind from it. So many chemical facts lately discovered, though seemingly of small importance, may, hereafter, prove of the greatest utility. For instance, the discoveries of the phosphoric acid in bones, and of the constituent principles of volatile alkali, seem as yet of no great consequence ; but I venture to predict, that when physic is rescued from its present obscurity, these will be equal to any that have hitherto been made. The utility of many facts may depend upon the discovery of a single one, which may throw light upon, and connect the whole. Hence, we find the necessity

cessity of well understanding and arranging such facts as we have in our possession, and likewise of increasing their number as much as possible; but in order to do this with facility and pleasure, and also to profit by them, it is necessary that we become perfectly acquainted with the true theory of chemistry, for false hypotheses can only tend to confuse and lead us further astray from the paths of truth, which alone ought to be the object and pursuit of true philosophy.

Nature has but one way of performing her different operations, therefore we may justly suppose that there is but one true mode of accounting for them, and consequently either the phlogistic or antiphlogistic theory must be false.

Des Cartes's vortical fluid appeared very plausible, and was generally received, until the immortal Newton, by his profound reasoning, pointed out



its inconsistency. Des Cartes grounded his hypothesis upon one phenomenon; the motion of the different planets from west to east. In like manner, Becher and Stahl founded their doctrine upon the phenomenon of combustion only.

Considering the knowledge they had in their days of the constituent principles of bodies, their hypothesis was very ingenious, although, in my opinion, as ill founded as that of Des Cartes. Speculative reasoning must ever fall to the ground when put to the test of experiment; such has been the fate of the Cartesian philosophy.

Although Lavoisier has not been as yet so successful as the great opponent of Des Cartes, yet he and his cotemporaries seem to promise, by their exertions, as sure and as lasting a theory as the Newtonian: even this has been opposed: why then should we be surprised that the antiphlogistic doctrine should

should meet with its opponents also? Notions early imbibed will not be readily exchanged for new ones; the slow but sure hand of time alone can dispel those clouds which never fail to eclipse truth at her early appearance.

The present controversy amongst philosophers depends upon the following questions: 1st, Whether water be or be not composed of dephlogisticated and light inflammable air? 2dly, Whether or no the condensation of dephlogisticated air, or its union to different bodies, does not depend upon one principle, common to all combustible bodies? Or, in other words, whether or no all bodies which burn or calcine, such as sulphur, phosphorus, charcoal, oils, metals, phlogisticated air, &c. contain the matter of light inflammable air as one of their constituent principles? One should suppose if these substances were composed of two prin-

a 4

ciples,

ciples, namely, a peculiar basis, and the matter of light inflammable air or phlogiston, that it would be possible to resolve them into these principles, more especially when we consider the great attraction of the matter of light inflammable air to fire; but the maintainers of phlogiston have not as yet been able to do this: therefore the only ground they have to build their hypothesis upon is, that these bodies unite to dephlogisticated air; then, according to their philosophy, dephlogisticated air has the property of uniting but to one substance in nature, except fire. If the above substances were simples, or even compounds, but destitute of the matter of light inflammable air, or phlogiston, the antiphlogistians cannot do any more than they have done already; for if sulphur were resolved into its constituent principles, and if these were

two



two airs, or more condensed bodies, different from any other with which we are at present acquainted, the phlogistians might still say that they contained phlogiston (or the matter of light inflammable air), if they even were the most simple bodies in nature, provided they had the property of uniting to dephlogisticated air. Then the antiphlogistians, in order to establish their doctrine, it seems, must prove the non-existence of that substance in bodies, whose presence as one of their constituent principles has never yet been proved. On this difficulty the phlogistic theory seems to rest.

Hence it appears that this doctrine, which has been generally received throughout Europe, almost the last half century, still stands in need of being substantiated; and also that the joint efforts of the first philosophers of the present age cannot fix their favourite doctrine upon a more firm

firm basis than the celebrated Stahl had done in his obscure days.

Thus seeing upon what principles the phlogistians and antiphlogistians maintained their different doctrines, and the impossibility of persuading us by experiments alone, from what only exists in our imagination, so prone we are to reconcile every phenomenon we see to our manner of thinking, I was obliged to have recourse to a mode of reasoning rather novel in chemistry. I have considered phlogiston as a substance chemically united to bodies in a solid state, and then inquired into the nature of such compounds, and whether the different phenomena in chemistry were consistently explicable on such principles. Again, I have endeavoured to find whether the same phenomena were as explicable by supposing the different bodies which unite to dephlogisticated air to attract it, independent of a common principle or phlogiston; by which

which means I have been enabled to make a fair comparison, and to draw, according to my judgment, just conclusions. If I have appeared more inclined one way than another, it is what the evidence of my senses and the love of truth compelled me to. I have not altogether depended upon the assertion of other philosophers, for I have frequently repeated almost the whole of the different experiments quoted in the following sections; otherwise I should not presume to offer my opinion to the public, knowing how differently we often judge of what is ever so well described to us, when we see it. In treating of the acids, I was obliged to have frequent recourse to the metals; for, in the present knowledge of chemistry, it is impossible to inquire into the nature and constitution of the one, without the assistance of the other. I have also been obliged to introduce several diagrams, in order to render what I meant to convey

the



the more intelligible; and indeed I thought it the surest mode of reasoning, and the most effectual means to come at truth \*.

I hope it will appear, that I have not taken pains to select facts in order to cast the scale in favour of the antiphlogistic doctrine; for, as truth was my object, I considered all facts equally efficacious in bringing her to light; therefore I made use of such as first occurred to me, and I thought were consistent with, and applicable to, the subject; in short, I preferred those that have been adduced in favour of the phlogistic theory; particularly such as have been advanced by Mr. Kirwan, in his Essay on Phlogiston, a work which I have frequently alluded to, as being intended to subvert the antiphlogistic doctrine.

\* The diagrams, placed at the margin, are very frequently to be read at the end of the first short line, as part of the sentence, otherwise the sense will appear very obscure.

Although

Although I adopted the antiphlogistic theory four years ago, and although every phenomenon which occurred to me since, tended to confirm the truth of that doctrine; yet, when I considered the number of able philosophers, namely, Cavendish \*, Priestley, Kirwan, Black, Higgins, &c. who persisted in the old doctrine, I began to waver in my principles, and my desire to minutely inquire into both doctrines daily increased; but knowing how inadequate I was to so arduous a task, and likewise how many there were who might have performed it so much better than myself, it was some time before I could summon resolution enough to begin; but my attachment to the science at length overcame every other consideration.

If my efforts should, in this enlightened age, be too feeble to do much good, I

\* I thought Mr. Cavendish had lately adopted the antiphlogistic theory, until a good part of this volume had been printed, as appears in the first section, page the 4th.

hope at least that they will not be productive of evil. I have written with conviction and without prejudice (otherwise it would be natural to suppose, that I would join my countrymen in defence of that doctrine in which I have had my early instructions in chemistry \*).

If I should be so unfortunate as to reason upon wrong principles, the sooner I am contradicted the better pleased I shall be; but if my arguments and inductions be just, if I even should meet with censure, it cannot last long; time, the parent of truth, will operate in my favour.

I fear I stand in need of much indulgence in both the style, and in the many oversights respecting the correction of the press, a task with which I have been totally unacquainted until the printing of these sheets commenced; and indeed I had an occasion to absent myself part of

\* I am indebted to Dr. Higgins for my first instructions in chemistry, who is a phlogistian.



the time, and the person who officiated for me was wholly ignorant of the subject, and equally as ignorant as myself with respect to the business of the press.

I have annexed an *Analysis* of the Human Calculus, which I hope will be acceptable as well to my medical as chemical readers. I was the more induced to publish it, as being delivered in to the Royal Society in the year 1787, and read at one of their spring meetings in the year 1788.

I have given an exact and true detail of the manner in which I have treated it; in order to give those who were better acquainted with chemistry than myself an opportunity of pointing out my errors, and to facilitate the labours of less experienced chemists, who may wish to prosecute the same subject; for, without mutual information, chemistry, as well as all other sciences, could never make any great progress.

As



As I have made my calculations according to Mr. Kirwan's table, being, in my opinion, the most accurate of any that has as yet appeared, I thought proper to insert it here, knowing that some of my readers will often have an occasion to refer to it; I have also added the heavy inflammable air, as I consider it a substance quite different from the light inflammable air.

*Mr. Kirwan's table of the absolute weight of 100 cubic inches of different kinds of air, and their proportions to common air.*

100 Cubic Inches.	gr.	Proportion to common Air.
Common air,	31	1000
Dephlogisticated,	34	1103
Phlogisticated,	30	985
Nitrous,	37	1194
Vitriolic,	70, 215	2265
Fixed,	46, 5	1500
Hepatic,	34, 286	1106
Alkaline,	18, 16	600
Light Inflammable,	2, 613	84, 3
Heavy inflammable,	34	1103



# ERRATA.

Page	Line
2,	12 from top, after lastly, <i>insert</i> a full point
3,	17, <i>dele</i> mixture of
11,	25, <i>read</i> molecules, and so elsewhere
15,	16, <i>dele</i> full point, and <i>insert</i> a semicolon
15,	three last lines, <i>read</i> Or do a dense and a rare atmosphere promote their chemical union, by easily blending and suffering them to approach nearer?
16,	7, <i>for</i> these <i>read</i> them
16,	8, <i>for</i> with <i>read</i> from
20,	16, <i>for</i> may <i>read</i> might
44,	13, <i>for</i> indecomposed <i>read</i> undecomposed
46,	20, <i>dele</i> that is.
59,	24, <i>for</i> dilute <i>read</i> diluted
83,	7, <i>dele</i> only
114,	16, <i>dele</i> 2-10ths and <i>insert</i> $\frac{4}{10}$
129,	14, <i>dele</i> comma
129,	15, <i>for</i> to <i>read</i> with
144,	10 from bottom, <i>for</i> loses <i>read</i> lost
154,	11, <i>dele</i> full point, and <i>insert</i> a semicolon
169,	ult. <i>insert</i> $\frac{1}{2}$
188,	5 from bottom, <i>insert</i> a comma after it
207,	2 from bottom, <i>dele</i> comma, and <i>insert</i> a full point
226,	3 from bottom, <i>for</i> barites <i>read</i> barytes



A

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## COMPARATIVE VIEW, &c.

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### SECTION I.

#### *Of the Composition and Decomposition of Water.*

**A**LTHOUGH Mr. Lavoisier had shewn the Decomposition of Water, in the year 1781, by a variety of ingenious and accurate experiments, as will appear in the sequel of this work; yet, his hypothesis was not received by any other philosopher; nor was he convinced himself, until the year 1784, when Mr. Cavendish removed all doubts, by uniting light inflammable air and dephlogisticated air, and shewing that the resulting compound was water.

B

Thus



Thus having proved by synthesis what the former philosopher suspected from analysis, the doctrine of Water was universally embraced by all the philosophers in Europe.

It undoubtedly is one of the most interesting discoveries that ever was made in Chemistry. 1. It enables us to account for several very important phenomena, which appeared before very mysterious. 2. It throws light upon vegetation, and the means whereby nature supplies the constant waste of our atmosphere. Lastly, It has thrown great light on the different stages of fermentation, which was not in the least understood before.

Some philosophers have lately suspected that water has never been either composed or decomposed in any of our processes. Mr. Kirwan supposes that water is formed by the union of inflammable air and dephlogisticated air only, when one or both are exposed to a red heat; but that in a lower heat they form fixable air\*. Mr. Lavoisier is of opinion, that one hundred parts of water contain eighty-seven of dephlogisticated air, and thirteen of light inflammable air, which is nearly seven to one.

According to Dr. Priestley's estimation of the weight of both airs, it is but five to one.

\* Essay on Phlogiston, p. 26.



However, from the variety of circumstances that may change the real specific gravity of these airs, I think we shall be nearer to truth if we say six to one, provided the airs be very pure. Two to one by measure appear to be the exact proportion.

Dr. Priestley supposes that the water produced by the condensation of inflammable air and dephlogisticated air, is only what was suspended and attached to them in their elastic state, and that their respective gravitating particles form a different compound, namely, Nitrous Acid. To ascertain this, he confined his mixture of airs with dry fixed alkali over mercury, in order to abstract from it as much water as possible.

Having thus prepared his mixture of airs, he found, after exploding them, that the product of water fell far short of the weight of both airs; and he observed a dense vapour after every explosion, which soon condensed, and adhered in a solid state to the sides of the vessel, which he afterwards found to be the Nitrous Acid\*. Though I do not doubt this indefatigable philosopher's facts, yet, I beg leave to differ from him in his conclusions. I think the facts he adduces are not

\* Phil. Trans. 1788.

only insufficient to ground his hypothesis upon, but do not in the least tend to contradict Mr. Cavendish's doctrine of Water and Nitrous Acid. Let us suppose four ounce measures of the mixed airs to produce, by inflammation, in their ordinary state one grain of water, and the same bulk of air, by exposure to lime or alkali, to be deprived of half a grain, and that, after condensation, the quantity of water produced not to exceed half a grain; are we to conclude from thence that water had not been formed? Besides, we are to consider that the specific gravity of air is altered in proportion to the quantity of water abstracted from it. Therefore, an accurate weight of both airs should be ascertained after they are deprived of their water, before we conclude that the weight of the water produced falls so much short of the weight of the airs employed.

That nitrous acid is often formed I have frequently experienced; but that it separates from the moisture produced, and, in a solid state, is what I could never observe nor suspect, considering the attraction of nitrous acid for water. I frequently inflamed several cubic inches of light inflammable and dephlogisticated air, and never observed, by the nicest test, the presence of an acid, when the airs worked



worked upon were pure, and when the inflammable air prevailed. But when I reversed the proportion, I always obtained nitrous acid in a single charge. When the dephlogistified contained one-eighth phlogistified air, I obtained nitrous acid in great abundance. Hence I infer, if we could procure dephlogistified air entirely free from phlogistified, that not a particle of any sort of acid would be produced. If nitrous acid should result from an union of light inflammable and dephlogistified air, why is not this formed during the slow combustion of a stream of inflammable air in dephlogistified air? I condensed, as shall be hereafter described, half a gallon of dephlogistified air by the continual flame of light inflammable air, and I could not detect the smallest vestige of any sort of acid. Then, I ask, what becomes of the airs? they must form some compound; for, from the quantity of fire disengaged, it is evident that a chemical union takes place. The difference in result between this process and that in which we use the electric spark may be easily accounted for. The intense heat produced in the latter process by the general and instantaneous inflammation of both airs, together with that of the electric spark, promotes an union be-



tween a portion of the dephlogisticated air and the phlogistic, which is always present in the purest respirable air. Whereas the languid combustion in the former experiment is insufficient to cause such an union. Why is not nitrous acid formed during the combustion of ether or strong spirit of wine, when the quantity of fixable air formed could never employ the whole of the dephlogisticated air expended, as evidently appears by the formation of fixable air by the electric spark? These circumstances, in addition to the many instances we have of the decomposition of water by calcination, fermentation, and vegetation, are sufficient to remove all my doubts respecting its constituent principles. That all elastic fluids hold a considerable quantity of water in solution, is well known to every body; but we are not to infer from thence, that water is a necessary ingredient in them, and that it is chemically united to the real gravitating matter of the different airs, particularly when we can extract the most part of it from them. Therefore, I do not see why we should say with Dr. Priestley, that inflammable air consists of inflammable air and water. We may as well say, that silicious earth (as water is separable from it) is silicious earth and water, or that sulphur is sulphur

phur and water, and so with all other known substances.

If the greater part of dephlogisticated air be water, and if iron be calcined in consequence of its union to water, as Dr. Priestley supposes, I would ask, Why is not inflammable air produced during the calcination of iron in dephlogisticated air, as well as when calcined by the steam of water? For the Doctor says, " But from the preceding experiments it appears, that by far the greatest part of the weight of dephlogisticated air is water; and the small quantity of acid that is in it may well be supposed to be employed in forming the fixed air, which is always found in the process of calcination." By this it is evident, that the Doctor does not allow the entry of dephlogisticated air into the calces of iron; and, according to himself, there was only the thirteenth of an ounce measure found in the residuum of seven ounce measures of dephlogisticated air absorbed by iron\*. Now seven ounce measures of dephlogisticated air are sufficient to form five, or at least four and a half ounce measures of fixable air. Therefore, I would ask, what becomes of this dephlogisticated air, or why was not nitrous acid formed?

\* Vol. vi. p. 120.

## SECTION II.

*Of the Composition of Acids.*

**I**T is to Mr. Lavoisier that we are chiefly indebted for our present knowledge of the constituent principles of the different acids; though it is true Dr. Priestley made the first advances towards it. It was by means chiefly of these substances that theoretical chemistry has made so rapid a progress these last ten years: so that we may very well say they have been the keys of philosophical chemistry. Mr. Lavoisier has shewn that dephlogisticated air is one of the constituent principles of all acids, and therefore called it the oxygenous principle, or the principle of acidity.

But yet we find that it is capable of uniting to bodies without possessing this character. Hence it appears doubtful to which of the principles we are to attribute this singular property. The different acid bases are sulphur, phlogisticated air, phosphorus, the matter of charcoal, regulus of arsenic, and the unknown basis of marine acid. Various are the opinions of the phlogistians respecting the nature of the union of dephlogisticated  
air



air to the above bases, though they all agree that they contain phlogiston. Some of these gentlemen suppose that the different bases are saturated with phlogiston, which uniting to dephlogisticated air, forms water, at the same time that another portion of dephlogisticated air combines with the basis, and constitutes the acid. Others suppose that these bases contain all the principles of their respective acids saturated, or as if it were enveloped by phlogiston; and that the air only separates this phlogiston by its superior attraction, whereby the occult acid is liberated.

Mr. Kirwan supposes that the dephlogisticated air unites to phlogiston, and forms fixable air, which, by combining with the basis, constitutes the acid. Thus he thinks that fixable air is the principle of acidity, and enters into the constitution of all acids. I shall endeavour to point out, in the following pages, the necessity of this last philosopher's doctrine towards the support of the phlogistic theory, and likewise his grounds for adopting such an hypothesis. Undoubtedly the doctrine of fixable air will enable phlogiston to stand its ground much longer than it otherwise would; for, it may be adopted where the other phlogistic doctrines are found insufficient; and again, in their turn, these  
may



may be introduced to explain such phenomena as are inexplicable in the former doctrine. Thus, by the mutual assistance of these different hypotheses, the phlogistians, by shifting their ground, may remain for some time in the field.

The antiphlogistians are of opinion, that sulphur, phosphorus, &c. are, according to our present knowledge of chemistry, simple bodies, which, when united to dephlogisticated air, constitute their respective acids. Thus the antiphlogistians consider all acids to consist of two principles only; one peculiar to each.

Mr. Lavoisier's Table of the affinities of the Oxygenous Principle. Mem. Par. 1782, p. 535.

<i>Bases.</i>	<i>Resulting Compounds.</i>
Basis of marine acid.	Dephlogisticated marine acid.
Reg. of man.	
Charcoal.	Fixed air.
Zinc.	Calx of zinc.
Iron.	Calx of iron.
Sulphur.	
Inflammable principle.	Water.
Nickle.	Calx of nickle,
Lead.	Calx of lead,
Tin.	Calx of tin,
	Phos.

Phosphorus.	Phosphorous acid.
Copper.	Calx of copper.
Bismuth.	Calx of bismuth.
Regulus of antimony.	Calx of antimony.
Mercury.	Calx of mercury.
Silver.	Calx of silver.
Regulus of arsenic.	Calx of arsenic.
Sugar.	Acid of sugar.
Sulphur.	Acid of vitriol.
Nitrous air.	Acid of nitre.
Principle of heat.	Dephlogisticated air.
Gold.	Calx of gold.
Smoaking marine acid.	
Nitrous acid.	
Black calx of manganese.	

Mr. Kirwan objects to the foregoing table.

1. Because he supposes charcoal, according to its precedency, should decompose water, in a boiling heat at least, considering that iron, which is placed lower, will produce inflammable air under the same circumstances. But the nature of charcoal should be first considered. Though its aggregate attraction appears weaker than that of iron, from its facility of pulverization; yet when reduced into powder, or small molicules, its ultimate particles may cohere with greater force. The frangibility of charcoal is in a great measure owing to the number of minute cavities which intersect

fect its texture, from the expulsion of the succulent part of the wood. Independent of the aggregate attraction, which certainly counteracts chemical union more than we are aware of, I think the ultimate particles of charcoal are furrounded with some repelling fluid, which defends them from the action of air and water; and the same may be said with respect to spirit of wine, ether, and oil: for they all have greater affinity to dephlogisticated air than phosphorus, which combines with it in the common temperature of the atmosphere. This, whether it be the electric fluid, common fire, or some other fluid, with which we are not acquainted, deserves attention. Nitrous air will rush into union with dephlogisticated air in any temperature, and yet sugar will not, though it deprives it of its dephlogisticated air. Pure calcareous earth, perfectly dried, will not attract marine acid air; and yet water, to which it has less affinity, will condense it, and enable it to unite to this. Light inflammable air and dephlogisticated air will not combine in their ordinary state but by the help of fire, either the electric, or a common spark; yet they will unite very readily when one or both are partially condensed. Thus nitrous air, which, as shall hereafter appear, is composed of dephlogisticated



cated air and phlogistic only, will condense hepatic gas. Hepatic gas, as I shall endeavour to shew in the sequel, is light inflammable air in its full extent, holding sulphur in solution. The sulphur is precipitated, and the residuum is dephlogisticated nitrous air. Here a portion of the dephlogisticated air of the nitrous combines with the inflammable air of the hepatic gas, and forms water. It cannot be said that this takes place in consequence of a double affinity. Phlogisticated air is with difficulty united to dephlogisticated air, though it attracts it with greater force than nitrous air. Iron moistened with water, and confined by mercury, will yield inflammable air. Iron, treated in the same manner, and confined with dephlogisticated air, will produce no inflammable air: but the air will be diminished. Iron will yield no inflammable air if it be confined in very dry dephlogisticated air, neither will the air be diminished, nor will the iron tarnish in any length of time. Hence it appears, that iron has no effect on air in a common temperature, but that it is the water which is decomposed, and that the dephlogisticated air and inflammable air unite at the very instant of its liberation, and re-compose water. These are difficult to be accounted for. All that



that we can say of them is, that a certain degree of condensation facilitates their union ; but this conveys no idea of the true cause. It may be said, that water condenses marine air in consequence of its capacity for fire. But why phosphorus, and not oils, or sugar ? or, why nitrous air, and not phlogistified, unite to dephlogistified, in a common temperature ? Or, again, why iron takes the oxygenous principle from water in preference to that in its aërial state, when the light inflammable air disengaged condenses it, is, in my opinion, very little understood.

It is true, all this may be justly attributed to fire, which, from its attraction to bodies, counteracts their chemical union to one another : but, from the following considerations, I think some other power must interfere. It is generally allowed, and justly, that nitrous air consists of dephlogistified air and phlogistic in the proportion of two of the former to one of the latter. The supposition of its containing phlogiston, I hope, will hereafter appear to be erroneous ; therefore every ultimate particle of phlogistified air must be united to two of dephlogistified air ; and these molicules combined with fire constitute nitrous air. Now if every of these molicules were surrounded with an atmosphere of fire  
equal

equal in size only to those of dephlogisticated air, 100 cubic inches of nitrous air should weigh 98,535 grains ; whereas, according to Kirwan, they weigh but 37 grains. Hence, we may justly conclude, that the gravitating particles of nitrous air are thrice the distance from each other, that the ultimate particles of dephlogisticated are in the same temperature, and of course their atmospheres of fire must be in size proportionable ; or else some other repelling fluid must interpose. The size of the repelling atmospheres of nitrous air thus considered, and likewise the weaker attraction of the molecules of this air to dephlogisticated air than that of the ultimate particles of phlogistic in their simple state. It is surprising to me, with how much more facility the former unites to dephlogisticated air than the latter. The decomposition of nitrous air, by the light inflammable air of the hepatic gas, is equally extraordinary, considering, as I said before, that the inflammable air is not in a condensed state ; and, therefore, combined with its natural portion of fire. Do atmospheres of equal density favour the union of their respective gravitating particles ? Or, do a dense and a rare atmosphere, by easily blending, promote their chemical union, by suffering them to approach

proach nearer? Or does the electric fluid interfere?

From the foregoing considerations, it seems to me that the attractive forces of bodies are not to be estimated by the facility of compounding, but rather by the difficulty of decomposing these again. Therefore, I beg leave to differ with Mr. Kirwan in his objections (page 24) to Mr. Lavoisier's Table of Affinities, until he adduces more substantial reasoning.

I think sulphur should be placed before light inflammable air, and manganese before charcoal, for reasons which will hereafter appear. Therefore, without making any alteration in Mr. Lavoisier's Table, I took the liberty of having these placed between both columns. In order to be the more explicit, I shall use the term aggregate attraction alone, in explaining that power which solid or less condensed bodies have of counteracting chemical union. Though, as I have observed above, I suspect some other force to co-operate with this: but I shall not presume to describe to others what I do not well understand myself. Thus, let us suppose charcoal to attract dephlogisticated air with the force of ten, and contrary powers, which I shall call the

the aggregate attraction, to resist this with the force of eleven. Let us likewise suppose iron to attract dephlogisticated air with the force of seven, and its aggregate attraction to counteract this with the force of six and seven-eighths. It would require greater heat to unite the two former than the two latter, though they have by far the greater affinity to one another. But when once the scale is cast in favour of the former, the rapidity of their union ought to be greater than that of the latter; which is really the case.



## SECTION III.

*On the Vitriolic Acid.*

**M**R. Kirwan is of opinion, that sulphur consists of a basis, or a radical principle, which, when saturated with phlogiston, constitutes sulphur, but with fixed air vitriolic acid; and when combined partly with the one and partly with the other, volatile sulphureous acid\*.

Let us for a moment allow sulphur to be what Mr. Kirwan supposes, that is, a certain basis saturated with phlogiston, and which, when exposed to dephlogisticated air, with due application of heat will unite to it, exhibit the phenomenon of combustion, and produce vitriolic acid. I ask Mr. Kirwan, What takes place in this process? He of course will say, that the dephlogisticated air unites to the phlogiston of the sulphur, and forms fixable air, which re-unites to the radical basis, and constitutes the acid.

According to Mr. Kirwan himself, water ought to result from an union of dephlogisticated air and phlogiston during the combustion

\* Essay on Phlogiston, p. 28.

tion of sulphur, considering that this cannot take place but in a red heat; therefore it appears to me, that his doctrine is a little contradicted in this process.

Other phlogistians, on the contrary, will say, that a portion of the dephlogisticated air unites to the phlogiston of the sulphur, and forms water, while another part unites to the basis of sulphur, and constitutes the vitriolic acid. I must confess, in this one circumstance, this last hypothesis appears to me to be the most rational and most flattering mode of supporting this imaginary theory.

Mr. Kirwan must acknowledge, that light inflammable air and dephlogisticated air constitute water; and, in his opinion, light inflammable air is pure phlogiston combined with fire, but when united to metals, the basis of sulphur, &c. that it is in a concrete state. Fixed air has never been known to result from an union of dephlogisticated air and light inflammable air in its pure state. I condensed upwards of one hundred cubic inches of dephlogisticated air by the combustion of light inflammable air in a jar inverted over lime water. The inflammable air was produced from iron entirely free from rust, and the vitriolic acid used was highly concentrated, and afterwards diluted with three times its bulk

of water. The inflammation of both airs took place during the extrication of the inflammable air, which passed through a copper tube seven inches long, with a bulb in the middle, which contained a small quantity of soap lees, both to retain any fixable air that may be separated from the iron, and likewise any vitriolic acid that may be mechanically forced up. The combustion was carried on at the extremity of this tube in a continual flame, and water trickled down the sides of the jar during the whole process; but not a particle of fixable air could I detect. I repeated the same experiment over distilled water, which I carefully boiled in order to expel any fixable air it may contain, and could not detect the smallest vestige of any acid. When these airs are combined by the electric spark, no fixable air is produced. During the deflagration of zinc in dephlogisticated air, no fixable air is produced, provided they be both pure. All philosophers agree that fixable air is an acid; then I ask, What are its constituent principles? Mr. Kirwan will no doubt say, Dephlogisticated air and phlogiston. Again, I ask, what the constituent parts of water are? He will say, as above, Dephlogisticated air and phlogiston. That is to say, they are the same things, but differently modified.

Let



Let us consider how widely different these two substances are in their properties, and we shall find that no modification could make this vast difference.

Fixed air will unite to different bodies, and change their physical and chemical qualities; even it will unite to water, according to Mr. Kirwan, its second self, and make a vast alteration in its properties. Allowing then, as I said before (and which is but a temporary indulgence), sulphur to be what the phlogistians suppose, a certain basis and phlogiston, where are the materials for fixed air? for, from what has been observed, it cannot be supposed that phlogiston, either in its aerial or dense state, will form fixable air. What answer can Mr. Kirwan make to this, though I allow him phlogiston? In my opinion, he must give up his fixed air, and say, with other phlogistians, that vitriolic acid is formed by an union of dephlogisticated air to the basis of sulphur, and that the phlogiston flies off; or adopt a more modern, and indeed the strongest argument in favour of phlogiston, the formation of water. I exposed near sixty grains or more of highly concentrated vitriolic acid and light inflammable air to heat sufficient to convert the whole into volatile sulphureous acid: the



process was carried on with a gradual heat, to prevent the distillation of the acid until decomposed. The residuum contained volatile vitriolic acid and light inflammable air, but not a particle of fixable air. If fixable air were one of the constituent principles of vitriolic acid, and if this again were composed of light inflammable air, or phlogiston, and dephlogisticated air; whether the inflammable air united to the basis of the sulphur, or whether it deprived the original phlogiston of the sulphur of its dephlogisticated air, fixable air ought to be produced; for the above process has been, according to Mr. Kirwan, very favourable to the formation of fixable air\*. When strong vitriolic acid was reduced to the same state by iron filings, fixable air was produced in very small proportion; which shews, that the fixable air did not result from an union of dephlogisticated air and light inflammable air, but must come from plumbago, or from some other impurity in the iron. If very pure alum be heated to ignition, it will yield dephlogisticated air and volatile sulphureous acid, but no fixable air. Mr. Kirwan will undoubtedly explain it thus, *viz.* That the basis of the sulphur de-

\* Essay on Phlogiston, p. 26.

prives the fixed air of its phlogiston, and that its dephlogistified air is disengaged, at the same time that the volatile sulphureous acid retains a sufficient quantity of fixable air and phlogiston to keep it in an intermediate state.

Here then the basis of sulphur seems to have greater affinity to phlogiston, than dephlogistified air has, or than it has to both dephlogistified air and phlogiston united; which even the phlogistians themselves will not allow. If it should be urged, that this decomposition is in consequence of the attraction of the different fluids for fire, light inflammable air should be produced; or, according to Mr. Kirwan, the fixable air should be converted into water, considering the degree of heat necessary for the process, and the basis of sulphur disengaged in its simple state.

Water could not be decomposed in this process. For, admitting the most plausible phlogistic hypothesis, that of the union of dephlogistified air to the basis of sulphur, while another part forms water, by combining with its phlogiston, a double decomposition must take place, *viz.* the basis of the sulphur must give up its dephlogistified air in consequence only of the mediation of fire; the wa-

ter then must be decomposed in consequence of the attraction of the basis of sulphur for phlogiston being superior to that of dephlogisticated air. Is it likely that the basis of sulphur should give up its dephlogisticated air so readily, at the same time that it unites to a substance of equal volatility, and to which it has less attraction? The dephlogisticated air of the water alone must be sufficient to prevent such an union. Sulphur gives up its phlogiston (if uniting to dephlogisticated air be such) in any degree of heat above ignition. Its phlogiston will even take a portion of their dephlogisticated air from metallic calces, notwithstanding two contrary powers, according to the phlogistic doctrine, oppose the union: for, if sulphur were a compound of phlogiston and a certain basis, how could its phlogiston take dephlogisticated air from the phlogiston of the metal? Is not here phlogiston to oppose phlogiston?

The phlogistians consider metallic substances to be composed of certain bases and phlogiston; allowing this, and likewise vitriolic acid, to be composed of three principles, phlogiston; the basis of sulphur, and dephlogisticated air; and the phlogiston and dephlogisticated air to be in the form of fixable air intimately united to the basis of sulphur;  
and



and likewise the metallic basis to attract its phlogiston with great force, as indeed it must, when the strongest heat cannot part them, notwithstanding the volatility of phlogiston. In this case, how can metals decompose vitriolic acid? for it cannot be supposed that the dephlogisticated air already united to phlogiston will quit it, to unite to the phlogiston of the metal: even the attraction of the basis of sulphur for both tends to render this improbable, as does likewise the attraction that must subsist on the other side between phlogiston and its metallic basis. It may be said, that the fixable air of the vitriolic acid unites to the metallic basis, at the same time that its phlogiston either passes off in an aerial state, or unites to the basis of the sulphur. If so, the metallic basis must have greater attraction to phlogiston and dephlogisticated air jointly, than to phlogiston alone; therefore, it must part with its phlogiston to unite to fixable air. If this should be the case, phlogiston in an aeriform state, or light inflammable air, could not deprive the metallic basis of its fixable air, even in the strongest heat; nor could it take dephlogisticated air from the metallic basis and its phlogiston; though it is true fire may weaken their union, and thereby enable the dephlogisticated air to quit the phlogiston  
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of the metal, to unite to the disengaged phlogiston. Is it likely that this should take place, especially when it appears that phlogiston and dephlogisticated air united will expel phlogiston from metals? Is it reasonable to suppose, that phlogiston will take dephlogisticated air from phlogiston, when the advantage and disadvantage of heat must be the same to both?

Let us now consider the other phlogistic hypothesis, that of the formation of water by the union of phlogiston and dephlogisticated air, while another portion of dephlogisticated air unites to the basis of sulphur, and forms vitriolic acid. Diluted vitriolic acid will calcine iron in any temperature, and light inflammable air is produced, which, in the opinion of the phlogistians, is the phlogiston of the metal combined with fire. What does the metallic basis unite with in preference to its phlogiston? If it only unites to that portion of dephlogisticated air attached to the basis of sulphur, then this basis might be obtained in its purity. Besides, if only dephlogisticated air united to the metals during solution, inflammable air would not be produced; for this is never obtained during calcination in dephlogisticated air. The basis of sulphur and its dephlogisticated air very likely

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unite to the metallic basis, and expel its phlogiston. But then, if this were the case, pure alkali, or calcareous earth, would precipitate the basis of iron in its pure state; a circumstance which has never yet taken place; for the precipitate is heavier than the iron, and it contains dephlogisticated air enough to saturate or condense the inflammable air extricated during the solution. Whence comes this dephlogisticated air? Not from the vitriolic acid; for it is not decomposed, as evidently appears from Mr. Lavoisier's experiment, who found that a solution of vitriol of iron required as much alkali to saturate it, as the same quantity of acid in its simple state. I have repeated this experiment, and found it to be so. Hence, I think the phlogistians must have recourse to water to enable them to attempt an explanation of the solution and calcination of metals in the vitriolic acid; and, in my opinion, they will then approach nearer to truth than before. Does the water itself unite to the metallic basis, and expel its phlogiston? The phlogistians must say it does, or allow the decomposition of water, which they are unwilling to do. If water alone were the chief agent in the calcination, as Mr. Kirwan himself observes,

observes\*, it would calcine iron with as much facility in its purity, as when mixed with vitriolic acid. Here, then, the metal is deprived of its phlogiston, and its basis united to dephlogisticated air: the acid is not decomposed, and the phlogistians will not allow the decomposition of water; and from what has been said above, the union of water itself is inadmissible; therefore, they must allow water to be decomposed. Does the dephlogisticated air of the water unite to the phlogiston of the metal, and let go its own phlogiston? Dephlogisticated air, as already observed, can hardly be supposed to quit one principle to unite to another of the same sort, which must be already intimately united to the metallic basis. Let us add to this, the attraction that must subsist between the principles of water.

The phlogistians, if they even must allow the decomposition of water, may still have recourse to one more mode of argument in support of their almost wrecked hypothesis; which appears to be but a plausible evasion of truth, and which is, that the metallic basis and its phlogiston attract dephlogisticated air jointly, with greater force than either separately; and in consequence thereof, that the phlogiston of the water must yield its dephlogisticated

\* Essay on Phlogiston, p. 99.



air to a superior force. Indeed, if this were the truth, we could not well account for the reduction of metallic calces by inflammable air in the strongest heat, when we suppose phlogiston to oppose phlogiston, and likewise when we consider the attraction of the metallic basis for both; which must be very considerable, when almost all the metallic calces will not yield either in the strongest heat, notwithstanding their volatility and attraction for fire. It is true, fire may weaken the union of phlogiston and dephlogisticated air to the metallic basis, but not so materially as to enable phlogiston to expel them both. In short, the phlogistic theory, taken in the most partial point of view, presents to me such numberless inconsistencies, that I should imagine its obscurity alone has prevented its fall long before this time.

Water will not apparently act upon iron in the common temperature of the atmosphere; but, diluted vitriolic acid will rapidly dissolve it, and inflammable air will be produced. This evidently shews, that the acid takes an active part in the calcination; and, from what has been already said, it still is found to contain all its principles. Whence, then, does the iron receive its dephlogisticated air? or, let the phlogistians explain, in  
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their doctrine, how the acid acts in this process. If highly concentrated vitriolic acid be used, very little inflammable air is obtained, but chiefly volatile sulphureous acid; and if heat be used for a considerable time, sulphur will be formed.

Let the phlogistians account, in their doctrine, for so material a difference in these two processes from the mere presence of water. I think they have remaining but one method of accounting for the latter; which is, that the basis of sulphur gives up its dephlogisticated air to the iron, at the same time that the iron yields its phlogiston to the basis of sulphur.

If this were the case, the same circumstance should take place in diluted vitriolic acid: besides, if the metal should exchange phlogiston for dephlogisticated air only, turbith mineral could not be reduced by the mere expulsion of it, provided phlogiston be a necessary principle in the constitution of metals. I think these facts tend strongly to prove the delusion of the phlogistic theory; for let us trace it which way we will, though it may flatter us in a few circumstances, it will lead us into a wilderness, where we lose sight of that concatenation of nature which  
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the adverse doctrine enables us to investigate without interruption.

What is the strongest proof of the existence of phlogiston in bodies? Inflammation when exposed to heat in atmospheric air. Is not the fire given out by the condensed air? Does dephlogisticated air unite to any substance but to that which contains phlogiston? According to the phlogistic theory, it does not. Is it inconsistent with the natural course of things, to suppose, that there are bodies which do not contain a particle of light inflammable air, and whose attraction for dephlogisticated air may be such as to combine with it (under favourable circumstances) so as to disengage its fire, dense enough to exhibit the phenomenon of combustion?

If the condensation of dephlogisticated air by the different bodies which yield flame and light were occasioned by the same principle common to them all, too great inertness would prevail between those bodies which contain dephlogisticated air, and those that are supposed to contain phlogiston; for phlogiston must counteract phlogiston, and thereby preserve a neutrality sufficient to resist numberless operations, as well conducted on the

the large scale of nature as in our laboratories.

Though we have not hitherto been able to decompose pure calcareous, argillaceous, siliceous, barytic and magnesian earths, or fixed vegetable and mineral alkalies, yet we suspect them to be compounds. Indeed, the very circumstance attending the increase of calcareous earth in the animal kingdom, is a strong instance of its being a compound, as likewise is that of fixed vegetable and mineral alkalies in the vegetable kingdom: but until we resolve these into their constituent principles, we must consider them as simple substances, and not attribute their different properties to one common principle. I think I may presume to say, that sulphur, phosphorus, phlogisticated air, and metals, are as simple bodies as the earths, and that we know as little of their origin or constituent principles.

The latter will unite to dephlogisticated air, but some with more facility than others, and present during the union nearly the same phenomena. But are we to infer from thence, that the same principle is common to them all, when the resulting compounds are quite different? The former (two excepted) will unite to acids, and present like phenomena;



menâ ; and may we not infer from this, with as great probability of truth, that the same principle which promotes a chemical union between the acid and any of these, is common to all, and which we may call the alkalinate principle ? Is not this last as rational an hypothesis as that of the principle of inflammability ? There are as strong grounds for the one as for the other.

If steam be passed over fused sulphur, light inflammable air will be obtained, as Dr. Priestley has observed. From whence does this air come ? The phlogistians will undoubtedly say that it is disengaged from the sulphur. If so, the basis of sulphur attracts water with greater force than it does phlogiston ; but will water and the basis of sulphur form vitriolic acid ? By no means ; though volatile sulphureous acid is formed in this process, which actually requires dephlogisticated air for its constitution ; a clear proof that water must be decomposed. I should like to know how the phlogistians can account for this decomposition. Let us suppose sulphur to be a compound of a certain basis and phlogiston, and water to be composed of dephlogisticated air and phlogiston : would the dephlogisticated air of the water quit its own phlogiston, to unite to the

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phlogiston of the sulphur? Unless some other power co-operated, and what can this be? The basis of sulphur unites to dephlogisticated air, and forms a compound in itself. Therefore it cannot be supposed that it could give any assistance to its phlogiston, which unites to the same principle, and forms a separate compound: on the contrary, we should expect that their mutual attraction to one another should prevent the decomposition of water. Let us suppose dephlogisticated air to attract light inflammable air with the force of 4, and the basis of sulphur to attract phlogiston or concrete inflammable air with the force of 3, and its aggregate attraction to be equal to one more, which must be nearly the proportion, considering that sulphur will not unite to dephlogisticated air in the common temperature of the atmosphere, but requires fire to remove its aggregate attraction. In this case water must be decomposed in consequence of the attraction of the basis of sulphur alone for dephlogisticated air, which must be more than equal to the contrary powers already mentioned (making an allowance for the attraction of aggregation), that is, it must exceed 7 to subdue them. The same statement may be observed with respect to the

calcination of metals by water, if we suppose these to contain phlogiston.

A good many more facts might be urged on this subject; but in my opinion enough has been adduced to convince an impartial reader, that all the phenomena above recited are only explicable by entirely leaving out phlogiston, and supposing sulphur to be a simple substance, whose ultimate particles attract dephlogisticated air with forces inherent in themselves, independent of phlogiston or concrete inflammable air, as an alkali does an acid, or gold and tin mercury; and likewise supposing the combustion of sulphur to be as simple a process as that of light inflammable air; that is, that there is no dephlogistication or formation of water during the union of the oxygenous principle to sulphur, as containing not a particle of light inflammable air in its constitution. I have often combined sulphur rendered perfectly dry, and dephlogisticated air likewise, deprived of its water by fused marine selenite in large proportion over mercury, and could never observe that water was produced. Indeed it may be said, that the volatile sulphurous acid, which is always the result of this process, may re-dissolve it; but this is not very

likely, when a small portion of water will deprive it of its elasticity.

According to Mr. Kirwan, 100 grains of sulphur require 143 grains of dephlogistified air to convert them into volatile vitriolic acid; but they require much more in order to become perfect vitriolic acid. Highly concentrated vitriolic acid contains 2 parts of dephlogistified air, and 1 of sulphur, exclusive of water.

One hundred and forty-three grains of dephlogistified air contain 41 of water, for lime will abstract 26 grains from it, and the remainder cannot be separated from it in its aerial state; therefore 100 grains of sulphur, making an allowance for water, require 100 or 102 of the real gravitating matter of dephlogistified air to form volatile vitriolic acid; and as volatile vitriolic acid is very little short of double the specific gravity of dephlogistified air, we may conclude, that the ultimate particles of sulphur and dephlogistified air, contain equal quantities of solid matter; for dephlogistified air suffers no considerable contraction by uniting to sulphur in the proportion merely necessary for the formation of volatile vitriolic acid. Hence we may conclude, that, in volatile vitriolic acid, a single ultimate particle of sulphur



phur is intimately united only to a single particle of dephlogisticated air; and that, in perfect vitriolic acid, every single particle of sulphur is united to 2 of dephlogisticated air, being the quantity necessary to saturation.

As 2 cubic inches of light inflammable air require but 1 of dephlogisticated air to condense them, we must suppose that they contain equal number of divisions, and that the difference of their specific gravity depends chiefly on the size of their ultimate particles; or we must suppose that the ultimate particles of light inflammable air require 2 or 3, or more, of dephlogisticated air to saturate them. If this latter were the case, we might produce water in an intermediate state, as well as the vitriolic or the nitrous acid, which appears to be impossible; for in whatever proportion we mix our airs, or under whatsoever circumstance we combine them, the result is invariably the same. This likewise may be observed with respect to the decomposition of water. Hence we may justly conclude, that water is composed of molecules formed by the union of a single particle of dephlogisticated air to an ultimate particle of light inflammable air, and that they are incapable of



uniting to a third particle of either of their constituent principles. The above notions of water and vitriolic acid being strictly kept in view, let us now proceed to enquire into the nature of sulphur and vitriolic acid, and their various effects on different bodies in the antiphlogistic doctrine.

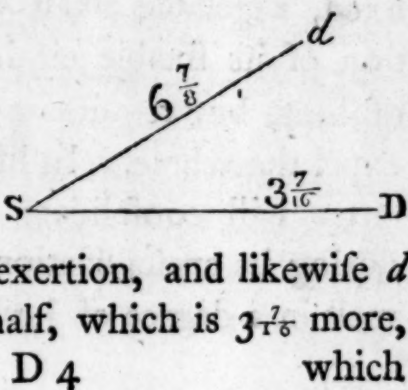
It has been already observed, that metals attract dephlogisticated air with greater force than sulphur, and that sulphur attracts it with greater force than light inflammable air. It has likewise been observed, that vitriolic acid and water, mixed in a certain proportion, will calcine metals with greater facility than concentrated vitriolic acid, and that water will have very little effect on metals in a common temperature. These facts, though they may appear contradictory in themselves when slightly considered, may be accounted for on the following principles, and are, in my opinion, inexplicable by any other means whatever.

Let us suppose iron or zinc to attract dephlogisticated air with the force of 7, sulphur to attract it with the force of  $6\frac{1}{2}$ , and light inflammable air with the force of  $6\frac{1}{3}$ . Let us again suppose these to be the utmost forces that can subsist between particle and particle. That is to say, in water dephlogisticated

gified air is retained with the above force, and likewise in volatile vitriolic acid, with the force already mentioned. It is unnecessary to introduce here the aggregate attraction which frequently preserves a neutrality between bodies, as, for instance, between water and zinc, or water and iron. Stating the attractive forces in the above proportion, which I am led to believe is just, from facts already observed, we should imagine that iron or zinc would calcine in water with greater facility than in vitriolic acid; and if some other circumstance did not interfere, it must be the case. This the following will in some degree illustrate.

Let  $S$  be a particle of sulphur,  $d$  a particle of dephlogistated air, which it attracts with the force of  $6\frac{7}{8}$ , and let the compound be volatile sulphureous acid; here the tie between  $S$  and  $d$  is greater by  $\frac{2}{8}$ , than that between the constituent principles of water, which is but  $6\frac{1}{8}$ . As the attraction of

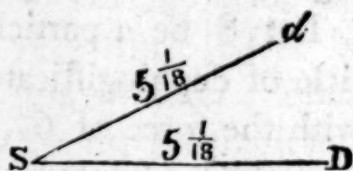
bodies is mutual, let us suppose  $S$  to possess one-half of this force, which is  $3\frac{7}{16}$ , and this to be its utmost exertion, and likewise  $d$  to possess the other half, which is  $3\frac{7}{16}$  more,



which will unite them with the above-mentioned force. Let us suppose another particle of dephlogisticated air *D* to have a tendency to unite to *S*, with the force of  $3\frac{7}{8}$ , in order to form perfect vitriolic acid: to receive *D*, *S* must relax its attraction for *d* one-half. That is, the force of  $3\frac{7}{8}$  will be divided and directed in two different points, which will reduce the attachment of dephlogisticated air and sulphur in perfect vitriolic acid to  $5\frac{1}{8}$ .

In order to more perfectly understand this, let *S* be sulphur, *d* *D* two different particles of dephlogisticated air united to it, with the different forces annexed to them. If *D* were taken

away, *S* and *d* would attract one another with the



force of  $6\frac{7}{8}$ , and when again restored would reduce this force to  $5\frac{1}{8}$ , and so alternately. This seems to be a general law. Mild, fixed, vegetable alkali will part with a portion of its fixable air in a moderate degree of heat, but requires a very intense heat to expel the whole. In like manner vitriolated tartar will consolidate a portion of water during its crystallization; in this state it will melt in a degree of heat below ignition, and  
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part with its water of fusion, and consolidate in the same degree of heat. If the mass be ignited, it will again fuse, and continue parting with water for some time; and when the whole is expelled, though the fire be on the increase, it will again consolidate, and require a much stronger heat to fuse it over again. Here we see that, in proportion as the alkali is deprived of a part of its fixed air, its power of retaining the remainder is redoubled, and that of the vitriolated tartar for water; for in the first fusion it parts with a portion of its water very readily, but during the second fusion it parts with the remainder with difficulty. Here we find, notwithstanding the volatility of water, the force of attraction subsisting between it and the salt retains it until it is red hot; and how great these powers must be, when we consider the mechanical force necessary to keep water in a condensed state, when simply exposed to the same degree of heat! I shall forbear mentioning several other circumstances of the like nature: let it suffice to say, that this explains the necessity of raising the fire towards the end of all chemical processes.

The true state of water and vitriolic acid being considered, when these fluids are mixed in different proportion, and then iron or  
zinc

zinc introduced, what are we to expect will take place? Undoubtedly the following decompositions. The iron will attack the dephlogisticated air of the vitriolic acid with the force of 7, which resists but with the force of  $5\frac{1}{8}$ , in preference to the dephlogisticated air of the water, which resists with the force of  $6\frac{5}{8}$ . We are not to suppose that the metal will attract *d*, in preference to *D*, but that it will influence them both equally alike; more especially when it presents surfaces enough. The sulphur being thus despoiled of its dephlogisticated air, but still preserving its extreme division, exerts the force of  $6\frac{7}{8}$  on the dephlogisticated air of the water, which it readily gains as meeting but with the resistance of  $6\frac{5}{8}$ , while the inflammable air is disengaged. The phlogistians may object to this by saying, that sulphur will not decompose water in the temperature of the above process. I will join them in this opinion; but be it recollected that fused sulphur, as already observed, will decompose water when brought in contact with it in the state of steam; and what promotes a decomposition here, but the interposition of fire between the ultimate particles of the sulphur, whereby its aggregate attraction is removed? But, if  
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this does not interfere in a low temperature, which is the case after the decomposition of vitriolic acid by metals, the decomposition of water will take place the easier; for, though fire removes the chief obstacle to the decomposition, it interferes a little itself. The ultimate particles of sulphur, when deprived of their dephlogisticated air, cannot recover more of this from the water, than is necessary to the formation of volatile vitriolic acid, see S  $\frac{67}{8}$  d, which being re-attracted by the calcined metal, acts as a solvent.

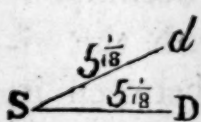
If concentrated vitriolic acid be used, the application of heat is necessary, and very little inflammable air is produced; but chiefly volatile vitriolic acid. The use of fire here is to remove the aggregate influence of the vitriolic acid, as well as to weaken that of the iron; both which circumstances favour the new union, or, as properly speaking, facilitate the decomposition. When water is mixed with the vitriolic acid, it interposes itself between its sluggish particles, which puts them beyond the sphere of their mutual influence; and thereby, though it is attracted by the vitriolic acid, answers the same purpose that  
fire



fire does; so that the solution goes on rapidly without the application of heat.

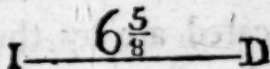
The volatile vitriolic acid disengaged, and the small quantity of inflammable air produced, when concentrated vitriolic acid is used, may, I think, be very satisfactorily accounted for in the following manner.

The first effort of the metal wholly deprives the particles of vitriolic acid in contact with it of their dephlogisticated air, and they instantly exert the force of  $6\frac{7}{8}$  on the dephlogisticated air of the neighbouring indecomposed vitriolic acid, which can only resist with the force of  $5\frac{1}{8}$ : they will not take D and  $d$  from S, but D or  $d$ , whichever happens to be most contiguous to them; therefore two portions of volatile vitriolic acid are formed. In order to render this the more intelligible, let S be an ultimate particle of sulphur, recently deprived of its dephlogisticated air, and still possessed of the power of  $6\frac{7}{8}$  to recover this again; and let



be a particle of vitriolic acid in the vicinity of S: will not S take D or  $d$  from S? and will not the volatile compounds  $\text{S} \xrightarrow{6\frac{7}{8}} d$   $\text{S} \xrightarrow{6\frac{7}{8}} \text{D}$  be formed? The latter will pass off in an elastic state, while the former,  $\text{S} \xrightarrow{6\frac{7}{8}} d$ , being nigher the metallic

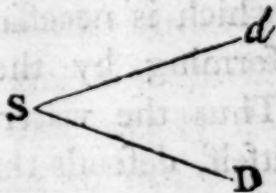
metallic calx, is attracted by it. As the most concentrated vitriolic acid contains a portion of water, part of this likewise is decomposed; hence arises the inflammable air. Let A be a particle of water, I and D its constituent principles; I inflammable air, and D



dephlogisticated air, com-

combined with the force of  $6\frac{5}{8}$ ; if A should be interposed between S, and

would not S the rather deprive I of D, than wait the approach of



the vitriolic molecule which is beyond its reach? particularly when the above-mentioned force of S is constantly rivetted or levelled, if I may use the expression, towards dephlogisticated air, in whatever compound, or in whatever state it meets with it, unless some other power counteracts it; and what can this be, but the union of the ultimate particles of sulphur to some other substance which attracts them more forcibly, or their own attachment to one another so as to form an aggregate? neither of which circumstances interferes here. In addition to the above explanation of the interference of the small quantity of aqueous particles in concentrated vitriolic acid, I need only say, that when  
this

this acid is so diluted as to afford only inflammable air, the particles of water, by surrounding these of the acid, or by the intermixture of their more numerous surfaces, are exposed to the influence of the sulphur, the instant it is deprived of its dephlogisticated air by the metal, and thereby prevent the formation of the volatile sulphureous acid, marked S——D, while S——d, which is necessary to solution, is constantly forming by the decomposition of water. Thus the water, though it is decomposed itself, defends the vitriolic acid, whereby we obtain inflammable air in such abundance.

From what has been said respecting the solution of metals in diluted vitriolic acid, we find that  $\frac{1}{3}$  more dephlogisticated air should be contained in the metallic solution, than is necessary to the formation of perfect vitriolic acid. That is, it contains that portion which the sulphur takes from the water, in addition to the quantity originally contained in the vitriolic acid; which the following circumstances tend to corroborate.

Fixed vegetable alkali will decompose a solution of vitriol of iron, and form vitriolated tartar, at the same time that the iron is disengaged of a dirty bluish colour, combined only with about  $\frac{1}{3}$  the portion of dephlo-



dephlogisticated air necessary for its thorough calcination. It could not receive this dephlogisticated air from the vitriolic acid, for this is united to the alkali in its perfect state. See



otherwise we should have a compound resulting from an union of the alkali to S—*d*,

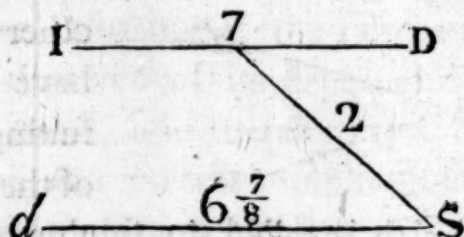
which is called the sulphurous salt of Stahl.

If a saturated solution of martial vitriol be exposed to dephlogisticated air, a yellowish calx is deposited, and in time nearly the entire of the iron is brought to this state. I frequently examined different calces of this sort well washed with hot water, and found that some contained vitriolic acid, and that others did not. If the solution be exposed to the air for a considerable time, it acquires an acid taste by the liberation of a portion of the vitriolic acid. Fixable air will likewise decompose this martial solution, as shall hereafter appear. Perfect vitriolic acid will have no effect on the perfect calx of iron, but volatile sulphurous acid will partially dissolve it.

These facts seem to correspond, and I think may be thus accounted for. Let I be iron; D dephlogisticated air united with the force of 7; let us suppose D to be the quantity

quantity necessary to saturate I, so as to form a perfect calx; let S be sulphur,  $d$  dephlogisticated air attached with the force of  $6\frac{7}{8}$ . Let us

suppose S to have a tendency to unite to more dephlogisticated



air; and let us likewise suppose, which is well known to be the case, a small attraction to exist between S and I. Let us state the whole sum of these forces between S, D, and I, to be 2; which power, though it will not separate I from D, or  $d$  from S, yet is sufficient to combine I—D to S— $d$  when in contact, and when no other power is to counteract it.

If the vitriolic solution above considered be exposed to dephlogisticated air, the following decomposition will take place, *viz.* another particle of dephlogisticated air will unite to S, which will counteract the attraction of I—D for S— $d$ ; therefore the separate compounds I—D and



will be formed. For the attraction of  $d$  for S, which I have already stated to be  $3\frac{1}{6}$ , is sufficient

ficient to subdue the power of 2, which united I—D and S—*d*. In order to prove this more fully, let the calx of iron I—D and perfect vitriolic acid be mixed; they will not unite; for I being saturated with D, can have no effect on *d* D; and S in like manner being saturated with *d* D, can have no effect on D. We are to consider the particles of dephlogisticated air D D *d* to have no sensible attraction for one another; and likewise the attraction of *d* D to S to be such as to more than counteract the attraction of S to I. For though S may be deprived of *d* D by a force not much superior to  $5\frac{1}{16}$ , yet it would require more than the force of  $10\frac{1}{16}$ , to separate S from *d* D, provided the latter were not influenced. Hence arise several very important phenomena in chemistry, which arrangement forbids me to introduce here; and which, from their being little considered, gave birth to the phlogistic theory.



I introduced some iron nails, free from rust, into strong volatile vitriolic acid; when it stood for a few minutes, it acquired a milky appearance, and the solution went on without ebullition or extrication of air. On

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standing



standing for a few hours, the solution acquired a darkish colour, and a black powder was precipitated. This powder, when collected and washed, put on red hot iron, burned partly like sulphur, and partly like charcoal dust, and the incombustible residuum was of a purplish colour. The filtered solution was perfectly neutralized, and free from the least sulphurous pungency. Its taste was strongly chalybeate, but not so disagreeable as that of the solution of iron in the perfect vitriolic acid, or in any of the mineral acids.

Nitrous acid dropped into the solution instantly produced a cloudiness, which immediately disappeared without ebullition, though volatile sulphureous acid was disengaged in its utmost degree of pungency. The vitriolic, marine, and acetous acids decomposed this solution, but caused no turbidness, nor was any inflammable air produced \*.

In order to know whether the sulphur

\* I would beg leave to recommend a trial of this preparation of iron in disorders that require the use of chalybeates; but as this presumption is rather founded on theory, I shall not take the liberty of saying any thing particular in its favour, until experience enables me to urge it with confidence.

was disengaged from the volatile sulphureous acid or the iron, I poured marine acid on the same nails, when light inflammable air and hepatic air were copiously produced, and likewise sulphur was deposited in its crude state. When I used vitriolic or the nitrous acid, no sulphur was produced. I tried different nails, and likewise iron filings, with the same result. These facts convinced me, that the sulphur was separated from the iron ; but that all sorts of iron contain sulphur is what I cannot pretend to know, as I have not tried steel or varieties enough of malleable iron. However I have strong reason to suspect, that sulphur has more to do in the different properties of iron than we are aware of. That iron should contain sulphur, notwithstanding the different processes it must necessarily undergo before it acquires malleability, considering the volatility of sulphur, points out the force of their attraction to one another ; and the separation of this again by volatile sulphureous acid, shews likewise the greater attraction of iron to sulphur and dephlogisticated air jointly. That volatile sulphureous acid should dissolve iron without the extrication of inflammable air or phlogiston, is a very strong instance of the fallacy

of the phlogistic doctrine\*. If volatile vitriolic acid were a compound of phlogiston, a certain basis and dephlogisticated air, a greater quantity of inflammable air should have been disengaged during the solution of iron in this acid than when the perfect vitriolic acid is used. Let us even suppose volatile sulphureous acid to be composed of the basis of sulphur, phlogiston and dephlogisticated air, which is the opinion of all the phlogistians, though they differ with respect to the modification of these three principles; and, likewise, iron to be composed of a certain basis and phlogiston: I would ask the phlogistians what becomes of the phlogiston of the iron during its solution? They cannot say it is disengaged in an aeri-form state, for there is hardly any inflammable air produced. Therefore, all they can say is, that the phlogiston of the metal, and that of the volatile vitriolic acid, are present in the solution; but this contradicts their own principle, viz. that metals must lose their phlogiston, in order to

\* A small quantity of inflammable air is produced, but it is so trifling, comparatively to what should be produced from the quantity of iron dissolved, that it is hardly worth noticing, and, in my opinion, proceeds from a portion of perfect vitriolic acid, which is generally inseparable from the volatile acid.



become soluble in acids. What principle is there in volatile sulphureous acid that can attract the phlogiston of the iron? The dephlogisticated air cannot unite to it, as being already united with phlogiston according to Mr. Kirwan. The basis of sulphur can have no influence over it, being united to phlogiston and dephlogisticated air; or, if even the basis of sulphur were to unite to the phlogiston of the metal, it must have formed sulphur, which is in itself insoluble, and incapable of holding metals in solution. Besides, if the quantity of phlogiston they imagine be present in the solution, nitrous air ought to have been produced on the addition of nitrous acid, or inflammable air on the addition of the marine acid; neither of which had been procured, though they displaced the volatile vitriolic acid, and united to the iron. A solution of nitrated iron thus prepared, and completely freed from volatile sulphureous acid, will yield a more perfect calx than vitriolated iron, when both are precipitated by pure fixed vegetable alkali. The nitre thus obtained will yield less dephlogisticated air, and more phlogisticated air, than the same quantity of common nitre, but in what proportion I cannot say. I am induced to suppose, that the difference of

purity is in proportion to the quantity of dephlogisticated air united to the precipitate. I am sorry I have not an opportunity at present to ascertain this, by a more accurate repetition of the experiment.

The solution of a metal in an acid without the production of inflammable air, and the decomposition of this again by nitrous acid without the production of nitrous air, is very well worthy of attention; more especially when we consider that nitrous acid is always partly decomposed during its union to metals in the common way. Surely these differences cannot arise from phlogiston; for if such a thing existed in metals, it would be as prevalent in the solution, when we know it did not make its escape, and likewise when it is evident that there can be nothing to envelope or protect it, as when the metal is introduced in its simple state into diluted nitrous acid. When I treat of nitrous acid, I shall have an opportunity of resuming the latter part of this subject; and, as I have said sufficient to answer my present purpose, I will postpone it until then.

The solution of iron in volatile vitriolic acid is quite clear, but when exposed to the air it acquires a brown colour in a very little

little time; indeed, the surface of the liquor changes colour in a few minutes. I exposed part of this solution to fixable air confined by mercury, and the same change took place: fixable air and dephlogisticated air mixed, affected this solution in a shorter time than either separately. From the effects of fixable air as well on this solution as on other preparations of iron, I am induced to suppose, that the brown colour of rust and of other calces of iron, is occasioned chiefly by fixable air,

I precipitated some iron from a common solution of martial vitriol, and washed it well. I put a part of this into perfect vitriolic acid, and another portion into the volatile vitriolic acid; they seemed very quiescent, and no solution appeared to take place. I closed both up very tight in two vials, and laid them by for two or three days, when almost all the iron was taken up. I filtered both solutions, and into the vol. vit. solution gradually dropped aerated volatile alkali, which threw down a bluish precipitate. Aerated volatile alkali, dropped into the other solution, disengaged a brown precipitate, which was instantly re-dissolved. I continued dropping in the alkali until the solution was saturated, when an orange-co-

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loured



loured precipitate was obtained; very little fixable air was produced, until the solution was nearly saturated. I think we may attribute the re-dissolution of the precipitate to fixable air: for the solution having a superabundance of vitriolic acid in it, the aerial acid was more copiously liberated than if it had been a saturated solution; so that the disengaged calx was so much the better supplied with this solvent. Mild, fixed, vegetable alkali precipitated the iron from the vol. sulph. acid of a darkish blue colour; it likewise precipitated the above solution of perfect vitriolic acid of the same colour. Why was not the iron precipitated by the volatile alkali from both solutions of the same colour? Or why did not the mild fixed alkali precipitate as perfect a calx from the latter solution as the volatile alkali did? Or why did not the aerial acid dissolve the precipitate from the volatile acid, so well as it did that from the perfect acid? And lastly, why was not inflammable air disengaged during the solution of the iron in the above acids? If the precipitate of iron from the vitriolic acid by fixed alkali be dried or exposed to air for some time, the vitriolic acid will only take up a small portion of it, for the most calcined part is left behind.

Hence

Hence we find, that a precipitate procured from a solution of iron in perfect vitriolic acid, dissolves as well in diluted vitriolic acid, as in the volatile vitriolic acid, without the production of inflammable air, though it is but  $\frac{1}{2}$  calcined, or in other words, dephlogisticated. Why is not at least one-half the quantity of inflammable air, or phlogiston, disengaged here, that is separated during the solution of simple iron in vitriolic acid? I think this is not consistently explicable in the phlogistic doctrine; at the same time that it is not only explicable in the anti-phlogistic theory, but likewise tends to prove the non-existence of phlogiston in iron, and to corroborate what has been already advanced relating to the solution of metals in vitriolic acid.

It has been already observed, that fixed vegetable alkali precipitates iron from the vitriolic acid, and that perfect vitriolated tartar is obtained, though the iron is found to be partly calcined. Therefore it appeared, that the water furnished the dephlogisticated air, and that the iron contained only that portion which it received from the water. It has likewise been observed, that this portion of dephlogisticated air, in addition to that contained in perfect vitriolic

vitriolic acid, is the greatest quantity that can be retained in the solution of iron, and that more dephlogisticated air will decompose it. But it has been shewn, that volatile sulphureous acid will dissolve iron without the extrication of inflammable air, and that the solution contains but  $\frac{1}{3}$  the portion of dephlogisticated air contained in the solution of iron in perfect vitriolic acid. This shews, though a small quantity of dephlogisticated air will promote the union and solubility of iron and sulphur, that more will do it better; but that a larger quantity will separate them. Then, if this calx of iron contains only that portion of dephlogisticated air taken from the water, and if this, in addition to the quantity contained in perfect vitriolic acid, be the *quantum sufficit* for holding iron in solution; no wonder that the union should take place without the production of inflammable air, if this be disengaged by the decomposition of water; but if disengaged from the iron, it is as remarkable we should not obtain it. If a larger quantity of dephlogisticated air were united to the above calx, it would then be, as already explained, insoluble in perfect vitriolic acid, on the same principle that a solution



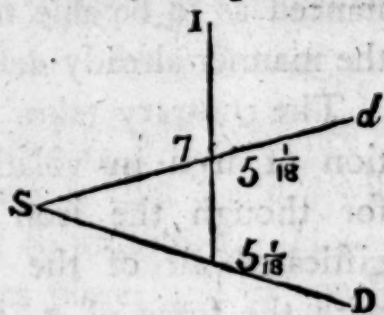
lution of martial vitriol is decomposed when exposed to air,

It may appear extraordinary that inflammable air is not produced during the solution of iron in volatile vitriolic acid, at the same time that it is so copiously disengaged during its solution in perfect vitriolic acid. This, I confess, puzzled me for some time before I could account for it. I think it is demonstrable in the following manner :

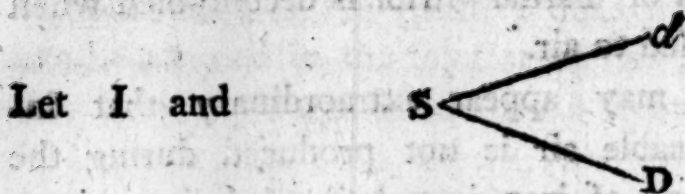
Let I be iron



vitriolic acid: let us suppose I to attract dephlogisticated air with the force of 7, and S, from its divided attachment, to retain its dephlogisticated air with the force of  $5\frac{1}{18}$ , as usual; and let us likewise suppose iron, from the closeness of its texture, to present a greater number of ultimate particles to a given surface than the vitriolic acid, particularly than the dilute vitriolic acid from the interposition of water.



Let

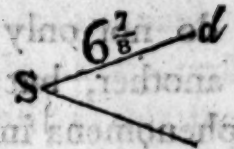


Let I and


S

be brought within one another's influence under these circumstances, and I will take  $d$  D from S; or S, in consequence of its attraction for I, which is but very small, comparatively to the opposite powers, will be forced along with D  $d$ . This latter is not likely to take place; for the force of 7, exerted at once by a number of the martial particles on D  $d$ , suddenly snatches them as it were from S, which cannot move with the same pace towards I; because, being in contact with water, it exerts its whole force on that compound. Therefore it is the violence and suddenness of the pull from the metal, and the velocity of the motion of D  $d$  towards it, that leaves S so circumstanced as to be able to decompose water in the manner already described.


The contrary takes place during the solution of iron in volatile sulphureous acid; for though the iron attracts the dephlogisticated air of the volatile vitriolic acid with the force of 7, it meets with the resistance

distance of  $6\frac{7}{8}$  S  as before de-

scribed; so that that superiority of force does not prevail here, as when perfect vi-

triplic acid is used. See S 

Indeed, if there were a greater inequality of force between S and I for  $d$ , S, from its attraction to  $d$ , and its tendency to I, would move with  $d$  towards I, and form the compound of S— $d$ —I, already described. Let S attract  $d$  with the force of  $6\frac{7}{8}$ : let I attract  $d$  with the force of 7, and let I attract S with the force of  $\frac{1}{8}$  only; the attachment of S to  $d$ , and likewise its tendency to I, make up the force of 7. There-

fore the force of 7, S 

subsisting between I and  $d$ , will influence S and  $d$  equally the same; so that S and  $d$  will move with equal pace to unite to I. Hence no decomposition takes place, and of course no inflammable air is produced. These two important



important facts do not only throw mutual light upon one another, but likewise upon several abstruse phenomena in chemistry.

Sulphur, in its simple state, will unite to mostly all the substances that vitriolic acid will. It unites to all the earths (the siliceous excepted), to the alkalies, to the metals (a few excepted), and likewise to the oils. The union of sulphur to the first class of these does not throw much light on its nature, as we are as yet unacquainted with their constituent principles.

The union of sulphur and volatile alkali admits of much more speculation than the former substances. It is now very well known, from the experiments of Mr. Berthollet and Doctor Austin, that volatile alkali is composed of phlogisticated air and light inflammable air. Sulphur will not chemically unite to inflammable air so as to consolidate it; though, as I shall hereafter be obliged to observe, it enables sulphur to combine with fire, and acquire an elastic state, whereby they are both held in solution, as sugar or Glauber salt is in water. Therefore, if sulphur be a compound of a certain basis and phlogiston, this basis must be fully saturated with phlogiston. It is not certain that volatile alkali will unite to  
any

any more light inflammable air than it is known to contain in its ordinary state, so that we must consider this likewise to be saturated with light inflammable air or phlogiston. Then, how can these substances unite, when their bases are already attached and saturated with that to which they have greater affinity, than they have to one another? Should not the same inertion prevail here, as when the perfect calx of iron is mixed with the perfect vitriolic acid; or when Glauber's salt is mixed with vitriolated tartar; or when selenite and baroselenite; or vitriol of zinc and vitriol of iron are mixed? Do not like these, substances of the same kind, and which have no sensible influence on one another, interfere between volatile alkali and sulphur? The same may be observed with respect to the union of sulphur to metals and oils.

The effects of oils on vitriolic acid correspond with the foregoing explanations. A small quantity of oil, or any other vegetable or animal substance that attracts dephlogisticated air, or, in other words, that is combustible, will partly decompose vitriolic acid, and discolour a large quantity. Vitriolic acid thus coloured, exposed to a strong heat, will emit volatile vitriolic acid  
in

in great abundance, and likewise fixable air, until it acquires its former transparency. Vitriolic acid, poured in small proportion on a large quantity of oil, will turn it to a darkish brown colour. This exposed to heat will yield fixable air and volatile vitriolic acid, with a small quantity of phlogisticated and heavy inflammable air; and, if the charge be urged with a tolerable strong heat, a small quantity of sulphur may be produced. Hence we may infer, that the acid is only deprived of a portion of its dephlogisticated air. Animal and vegetable inflammable bodies have certainly stronger affinity to dephlogisticated air than iron has, though they will not readily unite under any circumstance below the temperature of ignition. Oils, animal or vegetable, provided they be free from volatile alkali, will not mix or unite with water in a common temperature, but when diffused with it by agitation will assume a globular figure, and instantly separate from it again on standing: here the repulsive force between oil and water is evident. If oil and water be boiled under the common pressure of the atmosphere, no decomposition will take place; but if water be gradually dropped into boiling hot oil, inflammable air will be produced,



duced, as has been first observed by Mr. Lavoisier. The joint action of air and water can have no great effect on these, and if any at all, it must be in a great length of time. Suet and butter are not decomposed by water alone ; for I can affirm, that I have been present when a small tub of butter had been taken from under ground at least three feet deep, and which, from the situation of the soil and the decay of the wood, must have lain there for upwards of fifty years. It was surrounded with water, for it lay in a marshy soil. It had a disagreeable taste, and a spongy white appearance, but did not seem much changed in its chemical properties. From these, and similar facts too tedious to mention, we see the difficulty of uniting oils, butter, tallow, and charcoal to dephlogisticated air in a common temperature. In my opinion, as I have heretofore conjectured, these are protected from the action of air and water by some repelling fluid that surrounds their ultimate particles, independent of common fire, and which they are destitute of while enveloped in their respective kingdoms. For all animal and vegetable organic bodies

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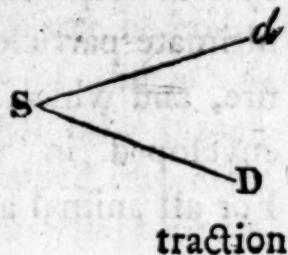
which

which contain these, are readily decomposed by exposure to air and water, or to water alone.

Considering these circumstances, it cannot be supposed that water should be decomposed, and inflammable air disengaged during the commixture of diluted vitriolic acid and oils. This reluctance oils have to unite to dephlogisticated air in a low temperature, in addition to their attraction for sulphur, opposes that sudden decomposition of vitriolic acid, or rapid separation of dephlogisticated air from the sulphur, by which, as in the instance of the solution of iron in diluted vitriolic acid, it is enabled to decompose the water.

When vitriolic acid, whether diluted or not, is mixed with oil, an ultimate particle of vitriolic acid influences with a certain force an ultimate particle of oil, while the latter attracts the vitriolic with the same force. The oil will not take  $Dd$  from  $S$ :

but from the joint at-



traction of S ——— D ——— *d* to oil, they will approach with equal pace, and combine. Thus this mixture more than mechanically, but not quite chemically united, may be resolved into the different fluids mentioned above. The particle of oil will retain D or *d*, and form fixable air; at the same time that S will retain *d* or D with its full force, and form volatile vitriolic acid.

Volatile vitriolic acid is not so readily decomposed by oils as perfect vitriolic acid, from the retention of its dephlogisticated air with so much the greater force. Therefore volatile vitriolic acid has not the property of charring oils as common vitriolic acid has, but it mixes with them, and forms a whitish or a saponaceous-like substance.

What has been said above, might be very well illustrated by minutely describing the various phenomena attending the different stages of that beautiful process of making vitriolic ether.

Here the vitriolic acid retains the oleaginous and aqueous part of the spirit of wine, while the most volatile part passes over in

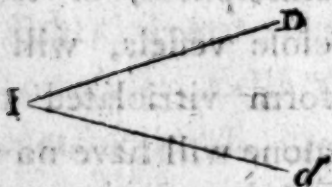


the state of ether, the nature of which cannot be discussed here. Ether of my own making, and which I carefully rectified from deliquiated fixed vegetable alkali, exposed to spontaneous evaporation, in the temperature of 37 or 40° of Fahrenheit's thermometer, left a small residuum of oil, water, and vitriolic acid. The quantity of vitriolic acid was so small, that I could only detect it by acetated barytes. However, it shews that vitriolic acid enters into the constitution of vitriolic ether. A portion of the same ether left no residuum in the temperature of 60°. A solution of terra ponderosa shewed no appearance of vitriolic acid in this ether. It appears to me, that ether is to light inflammable air, what the grosser oils are to the heavy which is favourable to the explanation of fermentation, &c.

Charcoal or oils will wholly decompose vitriolic acid when combined with fixed alkalies, and exposed to heat. Two circumstances favour this decomposition: 1st, The attraction of the inflammable matter for D *d.* 2dly, That of S for the alkalies. Liver of sulphur exposed to the atmosphere,

atmosphere, or to dephlogisticated air in close vessels, will attract the latter, and form vitriolated tartar; though sulphur alone will have no effect on dephlogisticated air, nor will alkalies in their simple state unite to it. On reflection, these circumstances appear very singular; but if we consider that the sulphur is united to the alkali in its extreme division, and that its attraction to dephlogisticated air is stronger than its attachment to the alkali, and likewise that the attraction of alkalies for vitriolic acid is greater than their attraction to sulphur, we may easily account for all this. The sulphureous salt of Stahl exposed to air, will unite to the dephlogisticated part, and form a perfect vitriolic salt; though volatile vitriolic acid in its simple state will not readily unite to dephlogisticated air. These facts clearly demonstrate, why alkalies take vitriolic acid in its perfect state from iron, at the same time that it is thrown down in a semi-calcined state; for, as I have before endeavoured to shew, the iron takes  $D d$  from  $S$ , by its superior attraction to dephlogisticated air, at the same time that  $S$  takes  $d$  from the water;

therefore S—*d* holds I



or the calx of iron in solution; from which circumstance we might imagine, that S—*d*, or the volatile vitriolic acid, should unite to the alkali, and form the sulphureous salt of Stahl, and that the iron should be precipitated in a more calciform state, that is, united with D—*d*, or double the quantity of dephlogisticated air which the precipitate generally contains. But finding that S—*d*, or volatile vitriolic acid united to alkalies or earths, attracts dephlogisticated air with greater force than when in its simple state, we can easily explain why the contrary takes place.

Sulphur partly acquires an aeriform state, when disengaged from the different hepars by acids. Liver of sulphur in its dry state is quite inodorous; but when moistened with water, it emits a strong hepatic smell, as Mr. Gengembre has observed. From this effect of water on liver of sulphur it is evident, that it promotes the disunion and



volatilization of a portion of the sulphur; but on what principle is not well understood. If this should take place in consequence of a decomposition of water, vitriolic acid ought to be formed, and of course vitriolated tartar; but it has not been found, to my knowledge, that liver of sulphur, either earthy or alkaline, has ever been vitriolated by the decomposition of water alone, but always requires the access of air\*. However, as the hepatic smell, or emission of the gas, is most predominant when only a small quantity of moisture is used, and on its first application, it may be said, that the dry hepatic compound has only then the power of decomposing water, and that the continuance of the smell is occasioned by a portion of the gas remaining in the compound from the difficulty of its expulsion. Iron filings will unite to sulphur in a moderate degree of

\* Since the above was written, Dr. Austin informed me, that liver of sulphur will not afford an hepatic odour when wetted in close vessels, and confined in mercury. It seems he has made several experiments on liver of sulphur, which he has given to the Royal Society.

heat, and form a black brittle mass, which on the addition of an acid will yield hepatic air in the utmost purity, and in great abundance, though it will not produce an hepatic smell when moistened with water, as calcar. pond. or alkaline livers of sulphur will. This shews the greater attraction of alkalies and sulphur jointly to dephlogisticated air than that of iron and sulphur, and likewise tends to prove what has been already said on the precipitation of iron by alkalies.

Dr. Austin has passed the electric spark repeatedly in hepatic air, and by that means precipitated all the sulphur without changing its dimensions. The residuary air was incondensable by water, and when washed had no hepatic smell. On burning this with dephlogisticated air, it appeared to be light inflammable air. This shews the constituent principles of hepatic gas, better than any other experiment that has hitherto been made on the subject. That sulphur is suspended in its natural state in light inflammable air, may be inferred from the above experiment; but whether in its extreme division is difficult to determine; or whether

whether it be chemically united to the inflammable air, or combined independently with its own atmospheres of fire, and mechanically mixed with this, cannot be satisfactorily proved. In my opinion it is mere solution, such as takes place between the neutral salts and water, or the alkalies and water, or sugar and water, &c. Though the facility whereby this is decomposed favours the above hypothesis, yet there are circumstances that are apparently against it; such as their united condensation in water, and their joint expulsion from it again. Upon what principle this attraction exists between bodies, has not yet been explained, or the difference between this and a chemical union ever defined. It appears to me that solution, that power whereby water dissolves aerial acid, alkaline air, vitriolic acid air; and that power whereby light inflammable air dissolves sulphur and phosphorus; and likewise that power whereby all the aeriform fluids dissolve water in their elastic state; and lastly, whereby water dissolves the neutral salts, &c. without changing their properties, is occasioned by a sort of intermediate attraction, not differing from  
chemical



chemical attraction but in its degree of force, and not at all different from that power whereby the heavenly bodies influence one another.

Dr. Austin fused sulphur in light inflammable air, in phlogisticated air, and in heavy inflammable air. The two former airs were not in the least altered; but the latter afforded one-third its original bulk of hepatic gas. It is remarkable, that the bulk of the air was not in the least altered in this process; and likewise that the residuary air, when the hepatic air was separated from it by water, should not appear in the least changed; for by inflaming it with a due proportion of dephlogisticated air, it yielded the usual quantities of fixed and phlogisticated air. The sulphur acquired a coally appearance in this operation; which induces me to suppose that it must have precipitated something from the air, the loss of which enabled the inflammable air to take sulphur in exchange.

The same philosopher passed the electric spark repeatedly in heavy inflammable air, until it increased nearly one-half in bulk; this he inflamed with dephlogisticated air  
over

over mercury by the electric spark. He likewise inflamed the same quantity of heavy inflammable air, not treated by the electric spark. By several repetitions of the above experiments, and from an accurate comparison of their respective residuums, he found that there was less fixable air, and a larger quantity of phlogisticated air in the former than in the latter; from which he concluded that heavy inflammable air is phlogisticated and light inflammable air, and that fixable air is composed of these two and dephlogisticated air. He likewise concluded, and justly, from the increase of bulk, and the small quantity of the heavy inflammable air that was decomposed, that if the entire were decomposed it would increase ten times its bulk. The conversion of heavy inflammable air into hepatic air without increase of bulk, and without any change in the residuary air, does not favour the above hypothesis: 1st, Because, as has appeared, and as shall be hereafter confirmed, light inflammable air is held in hepatic gas at its full extent. 2dly, Because the decomposed air should increase ten times in bulk.

3dly, Be-

3dly, Because no increase of phlogisticated air was found in the residuary air.

However, the Doctor supposes that volatile alkali is formed, whereby a portion of the inflammable air and the entire of the phlogisticated air remain united. Volatile alkali contains not much more by measure than four of inflammable to one of phlogisticated air; therefore the decomposed air should still increase six times its bulk. Besides, as this experiment was performed in dry mercury, the volatile alkali itself should remain in an elastic state.

As the Doctor intends to favour the public with these experiments, I shall not presume to say much on the subject. That heavy inflammable air contains light inflammable air, is certain from the formation of hepatic gas, as well as from its expansion by the electric spark; but I cannot avoid entertaining a doubt, whether the real matter of inflammable air with which dephlogisticated air forms fixable air, and which does not in the least differ from the ultimate particles of charcoal, be composed of light inflammable air and phlogisticated air. Indeed, considering that these are the  
constituent



constituent principles of volatile alkali, it appears rather improbable.

It seemed to me, for I was present, that something was precipitated from the air by the electric spark; for the lower part of the glass tube appeared black, while the sides seemed lined with a greyish substance. It likewise appeared to me, after the air acquired the expansion already mentioned, that a contraction took place by continuing the electric spark. This at least I can say with truth, that one hundred sparks at one time contracted it nearly one measure in eight or nine; but how much more it would diminish by continuing the operation, I cannot tell. I am almost persuaded to think, that the matter of charcoal in its extreme division, held in solution in light inflammable air and water, and combined with fire, constitutes the heavy inflammable air, on the same principle that sulphur and light inflammable air constitute hepatic gas; with this difference only, that the former gravitate more towards each other, which causes a greater condensation of the light inflammable air in the heavy than in hepatic gas, and of course

course a greater difficulty of decomposing it. Such likewise is the nature of phosphoric air, as has been observed by Mr. Gengembre, who I find, although I have not seen his analysis, has paid vast attention to this subject. Fire, it is true, is the first solvent in nature; next to this comes water; and next to this again light inflammable air, whether in its aerial or condensed state, such as in ethers and spirits. To this property of light inflammable air, I attribute partly the spirituous fermentation, and chiefly the result. From these, and other similar circumstances, my doubts arise respecting the constituent principles of the heavy inflammable air, although experience convinces me that it contains a small quantity of phlogisticated air. Thus far I have ventured to trespass upon the patience of my reader, thinking that the heavy inflammable air may tend to cast light on the nature of hepatic gas, and *vice versa*.

I mixed equal parts of hepatic air produced from iron filings and sulphur, and dephlogisticated air obtained from nitre. Seven measures of the former were absorbed

sorbed by water all to a small bubble, and the latter contained only one-tenth of phlogisticated air. Nine measures of this mixture were reduced by the electric spark to  $2\frac{1}{2}$ ; the nitrated solution of terra ponderosa condensed these to one-twelfth of a measure or less; and the solution did not appear in the least turbid, nor did any cloudiness take place on the addition of lime water. The residuum left unabsorbed was too small to be examined; but the portion condensed by the solution seemed by the smell to be volatile vitriolic acid. In order to be convinced of this, I inflamed another charge of the same airs, and transferred the residuum into a clean jar, which the sulphur deposited on the sides of the inflaming jar obliged me to do. To this I added an equal bulk of hepatic air, which instantly rendered it turbid, and reduced it to one-third, or a little more.

This assured me that the residuum was volatile sulphureous acid, and likewise that volatile sulphureous acid will not decompose nitrated terra ponderosa.

This experiment not only proves the constituent principles of hepatic gas, but  
 absolutely



absolutely proves what I have advanced respecting the proportion of the principles of volatile vitriolic acid. It has been shewn by Dr. Austin, that the solution of sulphur in light inflammable air, neither contracts nor expands it; therefore the above charge contained  $4\frac{1}{2}$  measures of light inflammable air, independent of the suspended sulphur. These  $4\frac{1}{2}$  ounce measures of light inflammable air, require at least  $2\frac{1}{4}$  of dephlogisticated air to condense them.  $2\frac{1}{4}$  measures more were expended in the experiment, two of which must be contained in the volatile vitriolic acid; and as the most part of the phlogisticated air disappeared, we may justly conclude, that the remainder of the dephlogisticated air, which is but one-fourth of a measure, was expended in the formation of nitrous acid. Hence we may conclude, that the two measures of volatile vitriolic acid contained two measures of dephlogisticated air; and as the specific gravity of volatile vitriolic acid, excluding the inflammable air, is the mathematical mean of the two fluids, we must suppose that only the sulphur of two measures

measures united to dephlogisticated air, and that the sulphur of  $2\frac{1}{2}$  measures was precipitated. Hence likewise we may infer, that the molicules of volatile vitriolic acid are surrounded with as large atmospheres of fire as the particles of dephlogisticated air, or at least that they are as far asunder; and that the number of the ultimate particles of sulphur in hepatic gas, are to those of the inflammable air as nine to five.

## SECTION IV.

*Of Nitrous Acid.*

**N**O subject in chemistry, until the decisive experiment of Mr. Cavendish, favoured the phlogistic doctrine more than the nitrous acid, from the variety of its modifications.

The large quantity of dephlogisticated air contained in this acid, and condensed by so small a portion of phlogisticated air, is very well worthy the attention of speculative men, at the same time that it enables us to account for the easy decomposition (more especially in part) of this acid; whereby it assumes the different appearances observable from the state of dephlogisticated nitrous air, down to the most perfect state of colourless nitrous acid. It is not an easy matter to ascertain exactly the greatest quantity of dephlogisticated air, that a given quantity of nitrous acid may contain. I always found nitre to vary in its product  
of



of phlogisticated and dephlogisticated air, and likewise in their proportion to one another. The purest nitre will yield, about the middle of the process, dephlogisticated air so pure as to contain but about one-thirteenth only of phlogisticated air. In the beginning, and nearly at the latter end of the process, air will be produced about twice better than common air. I mixed the different products of a quantity of pure nitre, and found by exposure to liver of sulphur that one-sixth was left unabsoꝛbed. This was the utmost degree of purity in which I obtained dephlogisticated air from nitre.

According to Mr. Lavoisier, 100 grains of nitrous acid contain  $79\frac{1}{2}$  of dephlogisticated air, and  $20\frac{1}{2}$  of phlogisticated air, which is not quite four to one. But his experiments contradict this; for whatever mode he adopted to decompose nitrous acid, it appeared that the proportion of dephlogisticated air was nearly as five, to one of phlogisticated air.

Mr. Cavendish has proved, that nitrous acid may be formed by taking the electric spark in a mixture of three parts of phlo-

gified air, and seven of dephlogified air, which is but  $\frac{1}{7}$  more of dephlogified air than nitrous air contains. This may apparently contradict Mr. Lavoisier's as well as my own estimation of the proportion of the constituent principles of nitrous acid when in its perfect state.

The red nitrous vapour contains three parts of nitrous air and one of dephlogified air, or one of phlogified and three of dephlogified air; but nitrous vapour may be formed with a less proportion of dephlogified air, and which, though it may not be so condensible as a more perfect nitrous vapour, yet will, when in contact with pure alkali, unite to it and form nitre, as was the case in the experiment of Mr. Cavendish.

The common straw-coloured nitrous acid contains more dephlogified air than the red nitrous acid or vapour; the proportion appears to be four to one; but the colourless contains about five of dephlogified to one of phlogified air.

Having once a charge of nitre and vitriolic acid in a green glass retort, I placed it in a sand-pot to distil; but the pot being  
small,

small, the edge came too near the retort, about a quarter of an inch or more above the charge, which before the process commenced, and when it acquired more than the heat of boiling water, cracked it all round in that direction. Being thus situated I was obliged to withdraw the fire, and, before the charge got cold, to ladle it into an earthen pan. I again introduced it into a fresh retort, and obtained from it nitrous acid nearly as colourless as water. As the vitriolic acid was not very perfect, I attributed the goodness of the nitrous acid to the purity of the nitre. Therefore I procured more of the same nitre in order to lay in a stock of nitrous acid; but to my surprise, though I used purer vitriolic acid than in the former process, my product of nitrous acid was of an high straw colour. Some months after, having an occasion for more nitrous acid, and recollecting the above circumstance, I mixed the vitriolic acid and nitre in due proportion, and exposed them in an earthen pan set in sand to nearly the heat of boiling water for half an hour or more, continually exposing fresh surfaces to the air. When the charge



was quite cold I introduced it into a retort, and distilled as colourless nitrous acid as the former. As the charge emitted no nitrous air during digestion, it must have attracted dephlogisticated air.

I would recommend this manner of treatment, to obtain nitrous acid in the utmost degree of perfection.

Before I proceed any farther on this subject, I think proper to mention the phlogistians' opinion of this acid, particularly Mr. Kirwan's, who has adopted a new phlogistic hypothesis respecting the modification of the constituent principles of the nitrous acid, and of all other acids.

This philosopher supposes, that 100 grains of nitrous acid in its pure colourless state, contain 38, .17 gr. of fixed air as its acidifying principle, 57, .06 of nitrous basis, and 4, .77 of phlogiston united to the nitrous basis; and that the nitrous basis contains  $\frac{1}{3}$  of its weight of phlogisticated air, and  $\frac{2}{3}$  dephlogisticated air, both in a concrete state, and that it has an affinity both to fixed air and phlogiston. Mr. Kirwan moreover supposes, that nitrous basis saturated with phlogiston, constitutes nitrous air,

air, and that 100 gr. of this basis take up nearly 22 of phlogiston. By this he means, that the principles of nitrous acid are fixed air, dephlogisticated air, phlogisticated air, and inflammable air, all in their concrete state.

According to this statement of nitrous acid, 100 grains of it in its pure dry state, provided the fixable air be decomposed, should yield about 60, .25 of dephlogisticated air, 15, .75 of heavy inflammable air, 19, .02 gr. of phlogisticated air, and 4, .77 gr. of light inflammable air\*. But if the fixable air should acquire an aeriform state, and so pass over in decomposing nitrous acid by heat, we should obtain the following proportion, viz. 38, .17 gr. of fixable air, 38, .04 of dephlogisticated, 19, .02 of phlogisticated air, and 4, .77 of light inflammable air, which in its aeriform state should occupy nearly the space of 200 cubic inches under the common pressure and temperature of the atmosphere; or if it should during the process be condensed into water, 100 cubic

\* The variation and increase of weight which the presence of water must necessarily produce in all aerial bodies are not here considered.

inches of dephlogisticated air must contribute to it: if this were the case, dephlogisticated air could never be obtained during the decomposition of nitrous acid.

I calcined 4 ounces of purified fixed vegetable alkali, to avoid any matter that may afford the inflammable principle of fixable air. On this I poured, diluted with distilled water,  $\frac{1}{4}$  more of the pure nitrous acid, obtained in the manner above described, than was sufficient to saturate it. Having digested it for half an hour in a matrafs, I charged it into a coated glass retort, and exposed it to a gentle heat, until all the water and superabundant acid were expelled. I then gradually raised the fire until the decomposition of the acid commenced. The first measure rendered lime water turbid, but the contraction was hardly measurable.

Measure 2 ditto.

3 ditto.

4 ditto.

5 ditto.

6 ditto.

7 less turbid.

8 ditto.

9 ditto

Measure



Measure 10 hardly rendered lime water turbid.

16 no appearance of fixable air, and continued so until the charge dissolved the retort. The quantity of fixable air obtained here could not amount to more than a cubic inch, and I make no doubt but this is an ample allowance for it, though 400 measures were obtained before the retort failed. As I made this experiment only with a view to ascertain the presence of fixable air, I attended to nothing else.

If fixable air be a necessary principle in nitrous acid, what became of it in the above process? If it had been decomposed, we should have obtained inflammable air, either light or heavy, neither of which was obtained. I frequently had an opportunity of examining the residuary alkali after the nitrous acid had been wholly expelled, and never could obtain from it either nitrous or fixable air, though there is generally an ebullition on the addition of an acid, occasioned by the generation of heat. I ask, what becomes of the 4.77 grains of pure phlogiston, or the matter of light inflammable air, contained, as Mr. Kirwan supposes,

poses, in every hundred grains of pure dry nitrous acid? As has been observed above, no inflammable air had been produced; and to suppose phlogisticated air to contain light inflammable air, is an hypothesis founded upon such weak grounds, that the phlogistians cannot produce one single instance to prove it. Even Mr. Kirwan himself, who is so strong an advocate for phlogiston, seems to doubt its presence in phlogisticated air; for he says, \* “ With respect to phlogisticated air, it must be owned we have no direct proof that it contains phlogiston, as no inflammable air has as yet been extracted from it, nor is it the general result of phlogistic processes; but since the nitrous acid formed of this air, and dephlogisticated air, was found strongly phlogisticated, and since the phlogisticated nitrous acid is constituted such by its union to nitrous air, it is evident that phlogisticated air must contain phlogiston, if nitrous air contains any.” Besides, according to Mr. Kirwan, the phlogisticated air in the nitrous acid contains its own proper phlogiston, together with the 4, .77 gr. of pure

\* Essay on Phlogiston, p. 40.

phlogiston; so that it cannot be said they were expended in forming phlogisticated air. Therefore the only way left to account for them is, that they united to a portion of dephlogisticated air, and formed water. 4, .77 gr. of light inflammable air require about 34 grains, or 100 cubic inches of dephlogisticated air to condense them into water, and there are but 4 gr. more of dephlogisticated air left, according to Mr. Kirwan himself. If this were to take place, we should obtain the following products from every 100 gr. of pure dry nitrous acid, viz. phlogisticated air 19, .02 gr. fixed air 38, .17 gr. water resulting from the phlogiston, and dephlogisticated air 38, .77 gr. dephlogisticated air 4 gr. How far this proportion corresponds with the products of the different airs obtained from nitre, I leave my chemical reader to judge.

Mr. Cavendish repeated his process for making nitrous acid on a tolerable large scale last spring\*. Dr. B——y, another gentleman, and myself, have had the pleasure of seeing it. The tube which confined the airs and soap-lees was accidentally

\* Anno 1788.



raised out of the mercury the day before, which gave me an opportunity not only of seeing but of tasting the nitre, which was in small crystals on the surface of the mercury. It does not appear that Mr. Cavendish used fixed air in the above process. But Mr. Kirwan attempts to obviate this by saying, that a sufficiency of fixable air may be suspended in the fluids worked upon. This could not be the case; for as Mr. Cavendish used soap-lees, he must necessarily pass his airs in it, so that no fixable air could be suspended. It may be said, that the soap-lees itself was not entirely free from fixable air. Even allowing this, it could have no share in the formation of the nitrous acid, as it must be formed by the union of the dephlogisticated and phlogisticated air, before they can unite to the alkali.

I mixed three parts of light inflammable air, and two of dephlogisticated air, which stood separately over lime 24 hours. The dephlogisticated air contained  $\frac{2}{5}$  of phlogisticated air. I inflamed 7 measures, or about 2 cubic inches of this, which left a residuum of  $\frac{1}{8}$  of the charge, which mea-

fired  $\frac{1}{4}$  of an inch. I added another charge to this residuum, and after inflammation it increased to half an inch. I inflamed a third charge, expecting a proportionable increase of residuum; but here I was deceived; for it contracted to  $\frac{1}{4}$  of an inch, being only the residuum of one charge. I continued the operation with nearly the like success, until the residuum got too large. I fired 12 charges in all, and the quantity of condensed liquor was by estimation about 4 gr. The surface of the mercury and brass conductors were much corroded. I let up a quarter of an ounce of distilled water, with about 2 drops of caustic fixed alkali, and left the whole to stand for a few hours. I then filtered the liquor, and evaporated it to dryness. I collected the salt, which weighed  $1\frac{1}{2}$  gr. it seemed not to be saturated, for it attracted moisture strongly; but ignited upon paper, it detonated like nitre. Thus it appears that nitrous acid had been formed in the above process, though I am certain that neither the inflammable air, nor the dephlogisticated air, contained an atom of fixable air. It cannot be urged that the dephlogisticated and inflammable

flammable air by their union furnished fixable air; for I hope I have already shewn that they constitute no such thing.

When I used very pure dephlogisticated air, no sensible portion of nitrous acid was produced, unless the dephlogisticated air predominated, and then there was very little procured. Hence we may conclude, that nitrous acid was formed in the above process, in consequence merely of the presence of phlogisticated air. When the above proportions were reversed, that is, when the inflammable air predominated, though the dephlogisticated air contained a large quantity of phlogisticated air, little or no nitrous acid was formed, which shews the superior attraction of light inflammable air to dephlogisticated air. Thus we find, provided the proportion be adjusted, that two processes may be carried on at once, viz. the formation of nitrous acid and water. I am confident, if we could get entirely rid of the phlogisticated air, that water may be produced in the above process in whatever proportion we mix our airs, without a particle of nitrous acid.

These



These facts must be sufficient to convince an unprejudiced person, that fixable air is not one of the constituent principles of nitrous acid, and that phlogisticated air is absolutely necessary to its constitution, and that the gravitating matter of light inflammable air, as some philosophers are pleased to suppose, is not one of the constituent parts of nitrous acid.

The formation of nitrous acid, without the presence of fixable air, or the materials to compose it, and the resolution of this again into its constituent principles, without the production of fixable air, must carry with them the utmost conviction. It may be said, that fixable air was produced during the decomposition of the above charge of nitre; but can it be supposed that 1, or even 8 cubic inches of fixable air, could render so highly acid as well as caustic, the quantity of nitrous acid that will saturate four ounces of fixed alkali? Besides, the fixable air obtained, was expelled at the commencement of the process; and before  $\frac{1}{10}$  part of the acid could be decomposed, a true sign that it was rather an extra production proceeding from

from some impurity in the nitre, than one of the constituent principles of the nitrous acid; for if fixable air were one of the constituent parts of this acid, we should obtain it equally copious at every period of the process, particularly when its extrication depends upon the decomposition of the acid, and likewise when we know that the alkali, after the decomposition of the nitre, contains no fixable air. Indeed the alkali, from its attraction to fixable air, if the nitrous acid could furnish this, should be obtained in a mild state; on the same principle that the alkali of foliated tartar is, after its decomposition. For though foliated tartar requires a strong heat towards the end of the process to completely decompose the acid, yet the alkali is always obtained in a mild state. Hence the reason why we obtain less fixable air in the beginning, than towards the latter end of the process.

Considering the universality of fixable air from putrefaction, combustion, and respiration, processes which must necessarily be carried on wherever mankind exists; and likewise considering, that all animal  
and

and vegetable substances contain more or less of this in a combined state, and that they are chiefly composed of one of its constituent principles, and that nitrous acid contains the other principle, it is not to be wondered at, that we should obtain more or less fixable air in all processes wherein nitre is used. Indeed, it is impossible for the most accurate experimentalist to guard against impregnations that may be productive of fixable air, 1st, Because the atmosphere is not only impregnated with aerial acid already formed, but is likewise loaded with moats that may adhere to our materials. 2dly, Our breath whilst we are preparing our charge, and insensible perspiration in addition to these, may all contribute to the generation of aerial acid.

I charged some ounces of common salt-petre, procured at the druggist's, into a coated glass retort. This I placed in a reverberating furnace; and when the air of the vessels was expelled, I examined the first measure, which rendered lime water turbid; but the contraction was scarcely measurable. The measure I used contained

H

about



about 8 cubic inches, and the proportion of fixable air was as follows:

Measures.	Fixable Air.
2 — — —	$\frac{1}{10}$
4 — — —	ditto.
6 — — —	ditto.
7 — — —	$\frac{1}{10}$
9 — — —	$\frac{1}{10}$
12 — — —	$\frac{1}{10}$
14 — — —	$\frac{1}{10}$
18 — — —	$\frac{1}{10}$
19 — — —	ditto.
26 — — —	$\frac{1}{10}$
30 — — —	$\frac{1}{10}$
40	scarcely measurable.
50	by conjecture, scarcely sensible.

60 no appearance of fixable air, and continued so during the whole process. The greater quantity of fixable air procured here than in the former process, proves that its production must be occasioned by the impurity of the nitre.

All spongy bodies, or the most compact substances when reduced to powder, will, though they may not have any chemical attraction to it, condense a small quantity of fixable air by capillary attraction. Even  
nitrous

nitrous acid will condense a small quantity of fixable air, though it will not enter into chemical union with it.

I deflagrated 2 ounces of pure nitre, prepared as above described, with about 7 dwts. of fresh made filings of zinc; and when the mass cooled, diluted vitriolic acid did not disengage a particle of fixable air from it. The same quantity of iron filings and nitre, after deflagration, yielded a small quantity of fixable air. If the fixable air proceeded from a decomposition of the acid in this last experiment, why was not the same quantity of fixable air produced when zinc filings were used? Or, if the fixable air was produced in consequence of an union of the dephlogisticated air of the nitrous acid and the phlogiston of the iron, why did not a similar union take place when zinc filings were used? for, if the one contains phlogiston, the other must. If the difference should be attributed to the greater quantity of phlogiston in iron than in zinc, I would answer, that this could make no difference, when there is a sufficiency in both to decompose the whole of the nitre. Besides, as I have observed before, light

inflammable air and dephlogisticated air have never been known to form fixable air. I would likewise ask, what becomes of the phlogiston of the metal during deflagration? for, according to Mr. Kirwan, the dephlogisticated air of nitrous acid is already attached to phlogiston.

If nitrous acid were composed of the principles Mr. Kirwan supposes; and likewise, if metals were composed of a certain basis and phlogiston, nitre would never be decomposed by metallic substances. The phlogiston of the metal being opposed by the phlogiston of the nitrous acid, can have nothing to do in the decomposition; and as the union of all the ingredients nitre is composed of, is dissolved when the dephlogisticated air is withdrawn from them, the metallic basis alone must overcome the following forces to unite to the dephlogisticated air, viz. 1st, The force whereby the nitrous acid and the alkali attract each other. 2dly, The force whereby the phlogisticated air attracts dephlogisticated air. 3dly, The force whereby nitrous basis attracts fixable air; and lastly, the attraction of their pure phlogiston to all these;



these; let us add to these forces, the attraction of the metallic basis on the other side to its own phlogiston. Therefore, if the metallic basis should attract dephlogisticated air so forcibly as to overcome all these collectively, can it be supposed that it would yield it again to phlogiston, or that it would exchange it for phlogiston? Undoubtedly not; though an allowance be made for the agency of fire in this circumstance.

If we consider nitrous acid to be composed of what in my opinion it really is, namely, dephlogisticated air and phlogisticated air, and metals to be composed of two principles, viz. earth and phlogiston, we may account for the decomposition of nitre upon a very rational principle; viz. the joint attraction of phlogiston and its metallic basis for dephlogisticated air. But we cannot account for the revivification of metallic calces again by inflammable air, upon this principle, considering that the phlogiston or light inflammable air of the metal must resist it, and likewise that the attraction of the metallic

H<sub>3</sub>      basis

basis itself to dephlogisticated air adds to this resistance.

It is true, it may be justly observed, that intense heat may weaken the union of the dephlogisticated air, the metallic basis, and its phlogiston, and thereby enable uncombined phlogiston, or light inflammable air, to unite to the former, or, what is the same in effect, to the metallic basis, and disengage its own phlogiston and dephlogisticated air in the state of water.

If we admit this mode of reasoning, it proves, that the metallic basis has greater attraction to inflammable air or phlogiston, than to dephlogisticated air alone, or than to dephlogisticated air and phlogiston jointly.

This, considered abstractedly, appears certainly very plausible; but, if we take a more extensive view of the subject, we shall find, that it will not correspond with other connected facts. For if iron had stronger affinity to phlogiston, or light inflammable air, than it has to water, or to dephlogisticated air simply, light inflammable air could not be produced from iron filings and water in a boiling heat, whether it  
comes

comes from the water or metal; or much less could this be produced by passing steam over the surface of red-hot or fused iron, particularly over the latter, as in this state it seems to retain its phlogiston with greatest force, if assuming a metallic state be such. Do not all the calcinable metals in the dry way, mercury excepted, unite to dephlogisticated air in the strongest degree of heat that our furnaces can produce? And will not inflammable air reduce these again to their metallic state in the same degree of heat? Therefore dephlogisticated air cannot be retained in metallic calces by the double force of the metallic basis and inflammable air, or its condensed phlogiston. If, as I believe I have already observed, the union of dephlogisticated air depended on the metallic phlogiston alone, inflammable air, by the assistance of heat, would decompose it. But, then, would this take dephlogisticated air from water? Indeed, I might as well have asked, if vitriolic acid would take fixed vegetable alkali from vitriolic acid? For surely phlogiston cannot take dephlogisticated air from phlogiston, more especially when it is already attached to the metallic basis.



These circumstances strictly considered, it appears to me, that in order to connectedly and consistently account for the decomposition of the different bodies into whose composition dephlogisticated air enters by metallic substances, sulphur and phosphorus, phlogiston must be left out.

If we consider metals as simple bodies, and of course destitute of the gravitating matter of light inflammable air; and likewise nitrous acid as a substance composed of phlogisticated and dephlogisticated air only, we may be able to account for the decomposition of nitre and nitrous acid, by the different metals, &c.

It has been observed, that metals have greater attraction to dephlogisticated air than sulphur, and sulphur than light inflammable air. Light inflammable air has greater attraction to dephlogisticated air than phlogisticated air has. Let us, in order to be the more explicit, suppose these different bodies to attract dephlogisticated air with the following forces:

Metals	—	—	7,
Sulphur	—	—	6, $\frac{1}{4}$
Light inflam.	—	—	6, $\frac{5}{8}$
Phlog. air	—	—	3,

Let

Let us likewise suppose fixed alkali to attract nitrous acid with the force of 4, which in addition to 3 enables the nitre to retain its dephlogisticated air with the force of 7. Hence filings of iron or zinc, though they will decompose the nitrous acid itself, will not decompose nitre in powder, or in solution, in a common temperature. The constituent principles of nitre attached with the above force, will recede from each other when exposed to heat by the interposition of fire, whereby their union or mutual influence is weakened; and this diminution of the force of their attraction, is in a duplicate ratio to the squares of their distances. Metallic substances, having their ultimate particles likewise removed from each other when exposed to heat, by which their aggregate influence is diminished, attract dephlogisticated air with the greater force.

These circumstances enable us to account for what takes place when we project nitre and zinc, or iron, or charcoal, and sulphur, into a red-hot crucible.

That famous philosopher, and accurate experimentalist, Mr. Lavoisier, having mix-

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ed and reduced into a most subtile powder 708,6 grains of nitre, and 93,52 of charcoal, pressed them into a copper tube, and after ignition introduced the tube, with its aperture turned down, under a jar of water, where the whole of the charcoal was consumed, and the nitre decomposed. The products were as follow:

Materials.		Products.	Cub. Inches.	Weights.
Gr.				
Nitre	708,6	Fixed air	708,25	329,33
Charcoal	93,52	Phlogist. air	195,56	59,8
	<hr/>	Caustic alkali	-	406,5
	802,12			<hr/>
		Total of the products		795,63
		Loss	-	6,49

Mr. Lavoisier was justly led to conclude from this experiment, that nitrous acid was composed of dephlogisticated and phlogisticated air, and that the latter was in the proportion of  $\frac{1}{3}$  of the whole of the acid; and likewise, that fixable air was composed of the matter of charcoal and dephlogisticated air.

The accuracy wherewith this experiment was performed, and the inferences drawn from it (particularly at a time when the constituent principles of nitrous acid were unknown),



unknown), shew the excellency of this great philosopher. There were 6,49 gr. missing, which must certainly be water. Indeed, considering the quantity of water in nitre, and likewise that the airs were produced in water, the loss of weight was very inconsiderable. In my opinion, 100 gr. of pure nitre contain, of

Caustic alkali	—	57 grains.
Dephlogisticated air	—	27
Phlogisticated air	—	6
Water	—	10

Total 100

From this statement I am induced to think, that the 329,33 of fixable air produced in the above process, contained the following proportion of its constituent principles, and water :

		Gr.
Dephlogisticated air	—	191,
Charcoal	—	89,52
Water	—	48,81

Total 329,33

59,8 of phlogisticated air contain, besides its real gravitating matter, 18 grains of water. The quantity of water held in solution

lution in both airs 66,81, in addition to 6,49, which was the loss of weight, accounts for the water of the nitre and charcoal. The following is the proportion of the different ingredients contained in the whole charge:

	Gr.
Dephlogisticated air —	191,
Charcoal — —	89,52
Water — —	73,30
Phlogisticated air —	41,8
Caustic alkali — —	406,5

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Total 802,12

In decomposing nitre *per se*, when the proper apparatus was used for collecting the different products, I always obtained water slightly acidulated; but, as this is produced in the beginning of the process, I think, if the quantity of water contained in nitre were retained until the whole was decomposed, the different fluids would dissolve the entire of it, or rather more, if they could be properly supplied with it. Therefore fixable air holds less water in solution, than the quantity of dephlogisticated air contained in it would in its simple state.

state. There is no possibility of ascertaining the exact quantity of water 93,52 grains of charcoal would hold in solution; for, during its conversion into an aerial state, a portion of the water is generally decomposed, more especially if too much be used, whereby we obtain fixable air and light, and heavy inflammable air, in various proportion. Hence we cannot actually prove the greatest weight 93,52 grains of charcoal would acquire, on its assuming an aerial state. The purest heavy inflammable air is that which is obtained from foliated tartar, and 5 parts of this require about 7 of dephlogisticated air to condense them into fixable air; from which I infer, that 93,52 grains of charcoal, in order to arrive at the above proportion, must hold much more water in solution in its elastic state, than 191 grains of the matter of dephlogisticated air, for there is very little difference in the specific gravity of these two airs.

Mr. Kirwan supposes, that the whole of the fixable air produced in the above process, does not result from the union of charcoal and dephlogisticated air; but that the nitre itself yields 91,86 grains of fixable air, as one of the constituent



ent principles of the nitrous acid; and according to him, 708, 6 gr. of nitre contain but 92 gr. of dephlogisticated air, besides the portion combined in the fixable air. 11,43 gr. of pure phlogiston, or the matter of light inflammable air, besides phlogisticated air, are intimately united to the above portion of dephlogisticated air, which at least are sufficient to convert 430 cubic inches, or nearly 146 grains, or, to make an ample allowance for water, 80 grains of the pure solid gravitating matter of dephlogisticated air, into water.

Thus, according to Mr. Kirwan, the quantities of combustible matter and dephlogisticated air contained in the above charge, exclusive of what was already combined in the form of fixable air, were in the following proportion, viz.

Charcoal	—	—	93,52 gr.
The gravitating matter of light	}		
inflammable air		—	11,43 gr.
Dephlogisticated air	—	—	92, gr.

Is this quantity of dephlogisticated air sufficient to saturate 11,43 gr. of light inflammable air, and consume 93,52 grains of charcoal? Undoubtedly not; and yet the

the whole of the charcoal was expended, and no inflammable air was produced. In my opinion, it needs no great share of sagacity to see into the fallacy of this doctrine. The above portion of combustible materials would require at least 261 gr. of the pure gravitating matter of dephlogisticated air, free from water, to consume or burn them; a quantity far exceeding the whole of the acid.

I fused a quantity of nitre in a small earthen tubulated retort, whose neck was elongated with a glass tube which immersed in water, and introduced into it 10,33 gr. of red-hot charcoal, which was exposed to a strong heat for half an hour. It was a whole piece, and the weight was ascertained as soon as it was taken out of the fire. When it got in contact with the fused nitre, a rapid deflagration ensued, attended with a copious extrication of fixable air. When I obtained about 40 cubic inches of air the deflagration ceased, and the charcoal was about  $\frac{2}{3}$  consumed. The fixable air was very pure, containing but 7 cubic inches of phlogisticated air. The difficulty of separating the alkali from the residuary charcoal

charcoal without waste, and the impossibility of consuming the entire of a quantity of charcoal, as it must be used whole in this experiment, render it impracticable to exactly ascertain the quantity of fixable air, a given quantity of charcoal would yield; for, as soon as the nitre next the charcoal is decomposed, the process ceases. In order to obviate this inconveniency as much as possible, I introduced a long and flat piece of charcoal weighing 10 grains, into a fresh charge of nitre; and as soon as the deflagration commenced, I kept the charge in continual agitation; which, with the large surface the charcoal itself exposed, enabled me to nearly consume the whole. The quantity of charcoal left could not exceed 2 grains. I obtained 80 cubic inches of air, 67 of which were fixed air, and the remainder phlogisticated air. These proportions induce me to suppose, that either the charcoal Mr. Lavoisier used contained phlogisticated air, or that I used purer nitre than he did; or, which is very likely, that the nitre was only partially decomposed in the above experiment, whereby phlogisticated air had been retained.

As



As the charcoal used in this experiment contained neither water, phlogisticated, nor fixable air, being exposed to a strong heat for a considerable time, (unless we admit that phlogisticated air is one of the constituent principles of charcoal), 67 cubic inches of fixable air, or 31 gr. contain 8 gr. of charcoal, and the remaining 23 gr. are furnished by the dephlogisticated air and water.

That the real matter of charcoal enters into combination with dephlogisticated air, is hardly to be doubted, however fixable air is generated; whether by the combustion of oils, spirit of wine, respiration, &c. or by uniting heavy inflammable air and dephlogisticated by the electric spark. Sulphur will decompose nitre with various results and phenomena, according to the proportion used; if two parts of nitre and one of sulphur be mixed, the nitre is decomposed with detonation, and volatile vitriolic acid, dephlogisticated air, and phlogisticated air, are produced; as Mr Berthollet has observed. The same philosopher found that one part of sulphur and four of nitre will not detonate, though the nitre is decomposed

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posed, and nitrous air produced. He distilled 120 grains of nitre, and 30 gr. of sulphur, and obtained 108,8 cubic inches of nitrous air, at the same time that the whole of the nitre was decomposed. This experiment is explained in the following manner, by Mr. Kirwan\*.

According to this philosopher, 120 gr. of nitre, contain 55 of acid, comprehending the water which is inseparable from it. Of these  $\frac{2}{3}$  or 36,6 gr. are nitrous basis, which require 6,6 gr. of phlogiston to convert them into nitrous air; the remainder of the 55 gr. of acid is fixable air: the following are his proportions, viz.

Nitrous basis	36,6
Fixable air	18
	<hr/>
	54,6

There are 2-10ths of a gr. unaccounted for. Mr. Kirwan having stated the principles of nitrous acid in the above proportion, supposes it to be decomposed by a double elective attraction, viz. the nitrous basis attracts the phlogiston of the sulphur, which he computes to be 6,6 gr. at the

\* Essay on Phlogiston, p. 58-9.

same time that the dephlogisticated basis of the sulphur unites to its fixable air; and as 18 gr. of fixable air, are too little to convert the dephlogisticated sulphur (as he is pleased to call it) into fixed vitriolic acid, they convert it into vitriolic air, which unites to the alkaline basis of the nitre. This is certainly a very ingenious mode of reasoning; but, in my opinion, it is not displayed in the cause of truth.

Mr. Kirwan, in the last statement of nitrous acid, left out the 2,73 gr. of pure phlogiston, which, according to himself, 55 grains of pure dry nitrous acid should contain, and which is united to the nitrous basis\*.

Therefore, counting this with the 6,6 gr. of phlogiston, which the basis takes from the sulphur, the 36,6 gr. of nitrous basis must be united to 9,43 grains of phlogiston, which should increase the weight of nitrous air proportionably; so that, instead of 43,2, we should obtain 46,03 grains of nitrous air.

Thus we find, according to Mr Kirwan himself, that 100 gr. of nitrous basis must unite to 29,37 gr. of phlogiston,

\* Essay on Phlogiston, p. 34.



though he says that 100 gr. of this, will take up but 22 of phlogiston. I think 2,73 grains of the matter of light inflammable air, in 55 gr. cannot be so very trifling as to be over looked in a compound of which dephlogisticated air constitutes the major part, more especially when we consider the quantity of dephlogisticated air which 2,73 of light inflammable air is capable of converting into water.

I think it is needless to say much more on the hypothesis of fixable air; it would be troubling my reader, and pointing out what, I flatter myself, he must be already convinced of. In my opinion, phlogiston must be entirely left out, in order to explain the different phenomena that attend the two last experiments. In the first of these experiments, Mr Berthollet used two parts of nitre, and one of sulphur: the nitre was decomposed, and the sulphur (to make use of the language of others) was dephlogisticated. Phlogisticated, and dephlogisticated air, were produced, but no nitrous air. When the same philosopher used four of nitre, to one of sulphur, vitriolic air, and nitrous air, were produced, and the

the sulphur was likewise dephlogisticated ; or (to make use of a more unexceptionable expression) vitriolated. In both experiments, it seems, the sulphur lost its phlogiston.

It appears extraordinary to me, if phlogiston should be one of the constituent principles, both of the nitrous acid and sulphur, that we did not the rather obtain nitrous air, or, if not nitrous air, phlogiston, or light inflammable air, when a greater quantity of sulphur was used, than a lesser. Mr. Kirwan attempts to account for this by saying, that the nitrous basis itself is decomposed when it meets with too much phlogiston.

If the nitrous basis were capable of uniting only to a limited quantity of phlogiston, and that a greater portion was disengaged in the process, the surplus should undoubtedly pass over in the state of inflammable air. Let us even, allow, for a short time, the nitrous basis to be decomposed, when we use one of sulphur, and two of nitre ; and let our quantities be 120 of nitre, and 60 of sulphur. According to Mr. Kirwan, 120 gr. of nitre contain 36,6 gr. of nitrous

basis, and 24,4 gr. of this is dephlogisticated air. 60 gr. of sulphur must part with 13,2 gr. of phlogiston, in order to become volatile vitriolic acid; which in addition to 2,73, make 15,93 gr. of phlogiston: therefore, the charge contained, besides the quantity contained in the volatile vitriolic acid, and fixable air, which we have nothing to do with at present, 15,93 gr. of phlogiston, and only 24,4 gr. of dephlogisticated air. It contained moreover, 18 gr. of phlogisticated air. The phlogisticated air is obtained in this process; but the 15,93 gr. of phlogiston seem to be totally lost, for no inflammable air is produced. The only rational mode of accounting for this lost phlogiston is, that it united to the dephlogisticated air of the nitrous basis, and formed water. Is it possible for 24,4 gr. of dephlogisticated air to condense, or either to convert into water or fixable air 15,93 gr. of the pure solid matter of light inflammable air? Besides, dephlogisticated air is obtained in this process; the quantity I cannot determine, although I have repeated the experiment. If we even leave out the fixable air supposed

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to be contained in the nitrous acid, and admit its weight of dephlogisticated air, which, with the dephlogisticated air of the nitrous basis, would amount to 42,4 gr. we should still find the quantity necessary to condense the phlogiston, short by 68 gr. at least. It cannot be said that this is converted into fixable air, from facts already adduced; besides, the sulphur is not more acidified here, than when nitrous air is produced; which could not be the case if fixable air were formed, and if this were the acidifying principle of the vitriolic acid. It is true, there is double the quantity of sulphur here, that is used when we obtain nitrous air; but let it be considered, that 48 gr. of the solid matter of fixable air should result from the above quantity of phlogiston, or the matter of charcoal, which is the constituent principle of fixable air.

These are my reasons for objecting, as well to Mr. Kirwan's doctrine, as to that of the phlogistians at large. In my opinion, the decomposition of nitre by sulphur may be accounted for more rationally in the following manner.

Although I do not think sulphur contains phlogiston, or the solid matter of light inflammable air, I by no means suppose it to be a simple body, but to be, relatively to our knowledge of chemistry, as simple as the earths, or the two fixed alkalies; all of which I make no doubt will be analyzed at some future period, when the science of chemistry will be more cultivated than at present, by men of genius, fortune, and leisure.

Hence, I conceive the ultimate particles of sulphur to unite in specie to these of dephlogisticated air, as phlogisticated air does during the formation of nitrous acid, without losing any thing but fire, which is always disengaged when a chemical combination takes place.

Of the constituent parts of the nitrous acid I have given my opinion, as deduced from facts. I have likewise supposed dephlogisticated air to be retained in nitre, with the force of 7, and sulphur to attract it with the force of 6 $\frac{1}{2}$ . I do not mean to intimate that these are their absolute forces; but, nearly the proportion they bear to one another. Thus, sulphur will not decompose

pose nitre, until exposed to heat sufficient to alter these forces. Nitre and sulphur mixed and comminuted, and put on hot iron, will not detonate, nor will the nitre be decomposed, though the sulphur will be burned out with a languid phosphorescent-like flame. Gunpowder also will not detonate, though the sulphur may be burned out with the same phenomenon, as may be seen by putting a little on a hot cinder, soon after it loses ignition. But, when nitre and sulphur are exposed to that degree of heat, which will so relax the chemical tie of the constituent principles of nitre, as to cast the scale in favour of the sulphur, it will then rapidly unite to the dephlogisticated air of the nitre, and present the phenomena of combustion and detonation.

Thus, two parts of nitre and one of sulphur will detonate when exposed to sufficient heat, at the same time that the nitrous acid is wholly decomposed. Sulphur will not unite to more dephlogisticated air, in the degree of heat necessary to conduct this process, than is sufficient to convert it into volatile vitriolic acid; or if it even did,



did, its attraction is not strong enough to take it from the nitre; as has been shewn in the third section of this work. Therefore we obtain, from the above proportion, volatile vitriolic acid, dephlogisticated air, and phlogisticated air; there is likewise some sulphur sublimed in the beginning of the process. When one part of sulphur, and four of nitre are used, the products are different; for then, the quantity of sulphur being very small, it presents but a few surfaces when mixed with the nitre, so that it can only take the portion of dephlogisticated air from the nitre which is over and above the quantity contained in nitrous air; thus the nitrous air, being deprived of its dephlogisticated air, is readily expelled from the alkali. The reason no deflagration takes place is, the particles of sulphur being but few, and interposed by the nitre, the quantity of fire disengaged by the more intimate union of dephlogisticated air to the sulphur, is insensibly dissipated; that is, it is not liberated in a sufficient degree of accumulation, to present the phenomena of light and combustion. The reverse takes place when a greater

greater quantity of sulphur is used: then the particles of sulphur being more numerous, and of course, closer to one another, fire is disengaged in a more concentrated state; at the same time that the whole, nearly, of the dephlogisticated air of the nitre is taken up. In order to deprive the nitre of the whole of its dephlogisticated air, it is necessary to use more sulphur than can unite to the dephlogisticated air. 1st, Because an ultimate particle of sulphur can only take an ultimate particle of dephlogisticated air from the nitre, whereby it forms volatile vitriolic acid. 2d, As every ultimate molecule of nitre contains, most commonly, four ultimate particles of dephlogisticated air, and one of phlogisticated air, which being enveloped thus in aggregates by alkali and water, are partly defended from the action of the sulphur.

Therefore, as the former cannot be so ultimately divided as the latter; if only that quantity of sulphur be mixed with the nitre, which will expose but surfaces enough to deprive the molecules of nitre of one half of their dephlogisticated air, nitrous air is produced; but if, on the contrary,

trary, a sufficiency be used to deprive the molecules of nitre of  $\frac{3}{4}$  of their dephlogistified air, we obtain phlogistified, dephlogistified, and vitriolic air.

If four parts of nitre, two of sulphur, and three of charcoal, be mixed and well powdered, they will burn rapidly, and emit a volatile vitriolic, and an hepatic smell. The entire of the sulphur is not here converted into volatile vitriolic acid. The charcoal having greater attraction to dephlogistified air, unites to the most part of it, while a portion of the sulphur unites to the alkali of the nitre. Hence arises the hepatic smell during the inflammation of gunpowder.

Charcoal detonates with nitre in various proportions, but will not disengage nitrous air in any proportion whatever. If nitrous air were produced, in consequence of a certain portion of phlogiston, as Mr Kirwan supposes, a less quantity of charcoal than is sufficient to decompose a quantity of nitre, should disengage it, if charcoal contains phlogiston. I think this may be explained on the same principle with the deflagration of sulphur and nitre. Charcoal and nitre  
distilled



distilled in various proportion, will afford phlogisticated and fixable air, but not a particle of nitrous air is produced. I would ask the phlogistians, why nitrous air is not procured here, when we obtain it from sulphur and nitre under the same circumstances?

Charcoal not only unites to a larger quantity of dephlogisticated air, than sulphur does, in order to become volatile vitriolic acid, but likewise attracts the portion necessary to its conversion into aerial acid with greater force. Thus charcoal mixed with nitre in a very small proportion will detonate, and fixable and phlogisticated air is produced. Every single molecule of charcoal (for we cannot reduce it into its ultimate particles by attrition) is capable of despoiling a single molecule of nitre of the whole of its dephlogisticated air; and this decomposition is so rapid, that the molecule of charcoal directs its whole attraction to the molecule of nitre, which first influences it; otherwise we should expect that the charcoal would take a portion of dephlogisticated air from different ni-  
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trous molecules at the same time; and thereby disengage nitrous air.

Metals decompose nitre, and present the same phenomena which charcoal does, but with a different result; for they produce little or no fixable air: and even the small quantity obtained from some metals, particularly from iron, is so liable to vary, that its presence appears to be accidental. Nitrous air is not produced during the decomposition of nitre by iron filings. Mr Berthollet distilled 472,5 gr. of nitre, with 236,23 of iron filings, and obtained 453,37 cubic inches of air, of nearly the same standard with atmospheric air\*. In short, all the imperfect metals will detonate with nitre, without producing a particle of nitrous air. As this is explicable on the same principle with charcoal and nitre, I shall not trouble my reader with it; but only observe, that if nitrous air were composed of nitrous basis and phlogiston, we could not but adjust the proportion of the nitre and metal favourable to the production of it, provided the metals contained phlogiston.

\* 2 pr. 217 mem. par. An. 1782, p. 495; and 1783, p. 85.

The regulus of arsenic put on red-hot iron, will burn with a flame. This does not indicate its greater attraction than other metals to dephlogisticated air, but the weaker adhesion of its ultimate parts to one another. The white calx of arsenic, although it is capable of uniting to more air, will not present the same phenomenon.

The regulus of arsenic will detonate rapidly with nitre. Equal parts of the white calx of arsenic and nitre, projected into a crucible hot enough to fuse them instantly, will not detonate. Two of nitre and one of the calx will not detonate. Three parts of nitre and one of arsenic exhibit a few brilliant sparks here and there; as do likewise two of arsenic and one of nitre, provided the crucible be very hot: but it seems to me to proceed from a few reguline particles, accidentally interspersed in the calx; otherwise the deflagration must have been more general. Nitrous air is produced from either of these proportions, but in a larger quantity when two of nitre and one of arsenic are used. Hence, we find that the regulus of arsenic *per se* will unite to dephlogisticated air, and present the phenomenon of com-



combustion, and that the calx will not; and likewise that the regulus will detonate with nitre, and that the calx will not; and lastly, that nitrous air is produced by the calx, and none by the regulus. Let us view these facts narrowly, and comparatively, and we shall find that they tend much to corroborate the foregoing explanation of deflagration, and the production of nitrous air.

That the regulus of arsenic combines with a certain portion of dephlogisticated air, and that on this union depends its calxiform state, is unquestionable; and likewise that the calx of arsenic will unite to more air, is beyond a doubt, as shall presently appear. Thus then, the regulus of arsenic, having greater attraction to dephlogisticated air, and being likewise capable of uniting to a larger quantity than the calx, as being already nearly saturated with it, wholly decomposes the nitre; and as a great number of the particles of dephlogisticated air unite with such rapidity and accumulation, in a given time, the phenomenon of combustion is produced.

When we take the calx, the result and  
appear-

appearances are different from the former ; because, being already combined with dephlogisticated air, it can only unite to a small portion of it, and this it even attracts with less force than the quantity necessary to its calcination. Thus, it can take only a portion of its dephlogisticated air from the nitre ; whereby, as has been already explained, we obtain nitrous air, at the same time that no deflagration takes place.

The phlogistians would explain the above facts by saying, that the different phenomena proceeded from phlogiston. Does the calx of arsenic contain phlogiston, uncombined to dephlogisticated air ? If it does, all the metallic calces contain phlogiston. Can any reason be assigned for supposing the calx of arsenic to contain phlogiston, but its property of uniting to more dephlogisticated air ? Or, is the production of nitrous air a sure sign that the bodies that disengage it, lose their phlogiston ? If so, the following facts are quite repugnant to it. The white calx of arsenic exposed to heat, in a crucible, will decompose nitrous acid, and disengage nitrous air very copiously. Thus, if nitrous acid in small

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tities be poured on it, from time to time, when every preceding portion takes due effect, the arsenic is acidified. In conducting this process, the fire should be gradually increased, in proportion as the arsenic draws near a saturation with dephlogisticated air; for the violent ebullition that takes place, particularly in the beginning, swells the charge, and puffs it over. The fumes should likewise be guarded against. Marine acid, mixed with the nitrous acid in small proportion, expedites this process. If the acid of arsenic, thus prepared, be exposed to a stronger heat than is necessary to its formation, it yields dephlogisticated air, and the arsenic is reduced to the state of a calx, and no fixable air is produced.

If the nitrous air were composed of nitrous basis, and the vast quantity of phlogiston which the phlogistians suppose, the calx of arsenic must be deprived of a large portion of phlogiston in the above process; and if the presence of this phlogiston were necessary to the reduction of the acid into a calx again, how is it supplied? In my opinion, this is inexplicable in the phlogistic doctrine, unless we admit the hypothesis  
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of fixable air ; the fallacy of which, I flatter myself, my reader is already aware of. Mr. Kirwan would explain the above process by saying, that the fixable air of the nitrous acid unites to the calx, at the same time that its phlogiston unites to the dephlogisticated basis of the nitrous acid, and forms nitrous air ; and that a stronger heat decomposes the fixable air, whereby its phlogiston remains attached to the calx, at the same time that its dephlogisticated air is expelled in an aerial state. As this mode of reasoning appears plausible enough for equivocation, it may be adopted in this one circumstance. But what correspondence does it bear to other connected facts ? A concatenation of facts, which regularly correspond with each other, will always bring truth to light ; although a number of facts ever so well understood or arranged, are seldom without a few, which may separately admit of a quibble, for those who wish to confound truth with falsehood, either out of a spirit of obstinacy, prejudice, or a desire of displaying their ingenuity. Hence arise so many theological controversies, as well as difference of opinion in

philosophy. But happily for mankind, the most ingenious projects, which the most fertile imagination can produce to suppress truth, generally appear, sooner or later, as so many evidences in her favour.

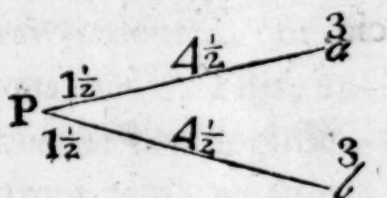
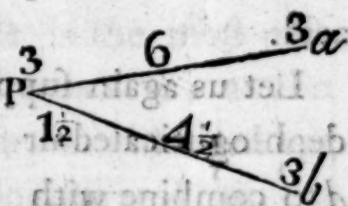
Having treated of the decomposition of nitre, I am now to inquire into the nature of nitrous acid in its simple state. In order to well understand the variety of changes which this acid is capable of undergoing by the mediation of different substances, it will be necessary, first, to be acquainted with the force by which its constituent principles are united.

In my opinion, the purest nitrous acid contains 5 of dephlogisticated to 1 of phlogisticated air. Nitrous air, according to Kirwan, contains 2 of dephlogisticated to 1 of phlogisticated air. According to Lavoisier, 100 gr. of nitrous air contain 32 gr. of phlogisticated air, and 68 of dephlogisticated air. I am myself of the former philosopher's opinion: I likewise am of opinion, that every primary particle of phlogisticated air is united to two of dephlogisticated air, and that these mo-  
lecules

lecules are surrounded with one common atmosphere of fire.

To render this more explicable, let us suppose  $P$  to be an ultimate particle of phlogisticated air, which attracts dephlogisticated air with the force of 3; let  $a$  be a particle of dephlogisticated air, whose attraction to  $P$  we will suppose to be 3 more, by which they unite with the force of 6; the nature of this compound will be hereafter explained.

Let us consider this to be the utmost force  $P$  that can subsist between dephlogisticated and phlogisticated air. Let us suppose another particle of dephlogisticated air  $b$  to unite to  $P$ , they will not unite with the force of 6, but with the force of  $4\frac{1}{2}$ ; that is, the whole power of  $P$ , which is but 3, will be equally divided and directed in two points towards  $a$  and  $b$ ; so that  $P$  and  $a$   $b$  will unite with the forces an-



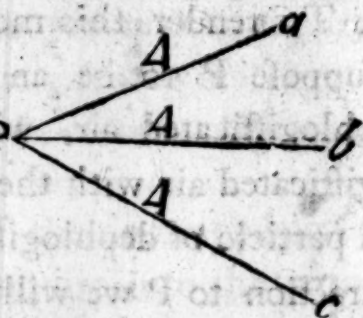
nexed to them; for the attraction of  $a$  and  $b$  to  $P$  meeting with no interruption, will

K 3

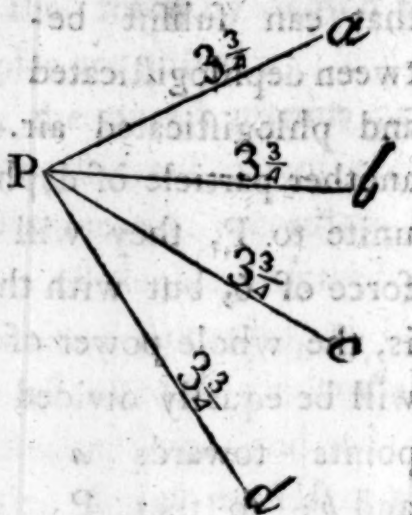
suffer



suffer no diminution. This I consider to be the true state of nitrous air. Let us now suppose another particle of dephlogisticated air  $P$  to unite to  $P$ , it will combine only with the force of 4, whereby  $a b c$  and  $P$  will gravitate toward one another. Such is the state of the red nitrous vapour, or the red nitrous acid.

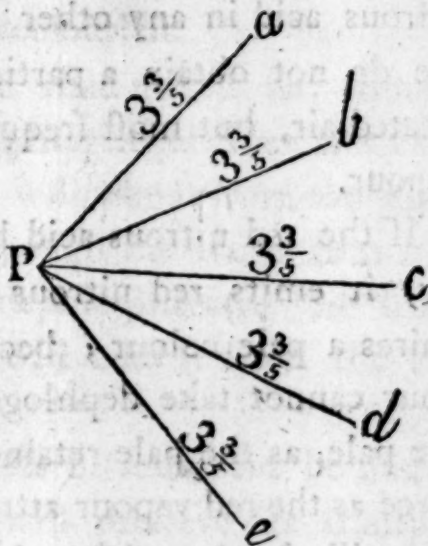


Let us again suppose a fourth particle of dephlogisticated air  $d$  to combine with  $P$ , it will unite only with the force of  $3\frac{3}{4}$ . This I think is the state of the pale or straw-coloured nitrous acid.



Lastly,

Lastly, let us suppose a fifth particle of dephlogisticated air *e*, to unite to *P*, it will combine with the force of  $3\frac{3}{5}$ , so that *a b c d* and *e* will each gravitate towards *P* as their common



centre of gravity. This is the most perfect state of colourless nitrous acid; and in my opinion no more dephlogisticated air can unite to the phlogisticated air, as having its whole force of attraction expended on the particles of dephlogisticated air, *a b c d e*. This illustrates the nature of saturation. Thence we find that dephlogisticated air is retained with less force in the perfect or colourless nitrous acid, than in the straw-coloured, or in the red, or in nitrous air. This explains the easy separation of dephlogisticated air from perfect nitrous acid, when exposed to the sun, or even to an artificial light or heat, at the same time that the

nitrous acid is coloured\*. If we expose nitrous acid in any other state to the sun, we do not obtain a particle of dephlogisticated air, but most frequently red nitrous vapour.

If the red nitrous acid be exposed to the air, it emits red nitrous vapour, and acquires a pale colour; because nitrous vapour cannot take dephlogisticated air from the pale, as the pale retains it with as great force as the red vapour attracts it. Nitrous air will deprive either the straw-coloured or colourless nitrous acid of a portion of their dephlogisticated air. The former, as Dr. Priestley first observed, acquires an orange colour, on combining with a portion of it; but, on uniting to more nitrous air, becomes green; and lastly, when saturated with it, acquires a red colour, and assumes the state of vapour. Nitrous air will not deprive the red nitrous acid of any portion of its dephlogisticated air, on the same principle that the red nitrous acid

\* Dr. Priestley found that dephlogisticated air was produced from nitrous acid, by passing the electric spark in a small quantity of common air confined in it. Vol. VII. p. 339.



will not decompose the pale nitrous acid, or the pale, the colourless.

Hence we find that nitrous air, though it cannot take dephlogisticated air from the red nitrous acid, will take it from the pale; and likewise, although the red nitrous acid will not take dephlogisticated air from the pale, that it will take it from the colourless.

If the colourless nitrous acid be mixed with water, it will preserve its transparency; but the red nitrous acid treated in the same manner, will acquire a blueish green colour. Water in this case condenses nitrous vapour so much, from its attraction to it, that it has the same effect as if a portion of it had been expelled.

Having premised thus much on the different stages of nitrous acid, I shall now proceed to the decomposition of it again, and endeavour to explain it in as few words as perspicuity will allow me.

If a metal be introduced into the red, pale, or colourless nitrous acid, it will be calcined, and nitrous air will be extricated; that is, it will deprive the nitrous air of that portion of dephlogisticated air necessary

sary to its condensation, or to the formation of nitrous acid. The metal deprives the particles of acid in contact with it, of the whole of their dephlogisticated air. The force of 7, with which we have supposed metals to attract dephlogisticated air, being so much superior to  $3\frac{3}{4}$  if we make use of the colourless, or to  $3\frac{1}{4}$  if we use the pale, together with the number of ultimate surfaces a metal must present, deprives the phlogisticated air (of the nitrous acid) of its dephlogisticated air, with such quickness, that it is at once left destitute of both fire and dephlogisticated air; but before it has time to collect an atmosphere of fire, which would prevent a second union, it exerts the force of 3 on its neighbouring particle of acid, which as yet did not reach the metallic influence, and thereby recovers that portion of dephlogisticated air necessary to the formation of nitrous air. This again, in passing in the acid, if it be the pale or colourless, will recover air sufficient to form nitrous vapour, or red nitrous acid. Thus it is, when first a metal is introduced into the pale or colourless nitrous acid, though a solution takes place, that little or  
no

no nitrous air is produced, until the acid is coloured. As the metal, after it is calcined, requires red nitrous acid to hold it in solution (for perfect nitrous acid will not do, as shall hereafter appear), the nitrous acid, which the phlogisticated air deprives of a portion of dephlogisticated air, unites to it.

The foregoing explanation may appear, at first sight, more speculative than real. But does not the decomposition of nitre by metallic filings, whether these be deflagrated in a red-hot crucible, or distilled by a more gentle and gradual heat in a retort, tend to confirm it? Is not the acid completely decomposed here, whatever proportion of the materials be used? In this latter case, the metallic surface deprives the nitrous molecules, in contact with it, of the whole of their dephlogisticated air; by which the phlogisticated air, as having no sensible attraction to the alkali, is disengaged in its simple state, if uniting to fire be such; for its attraction to dephlogisticated air is not strong enough to recover any portion of it from the joint force of phlogisticated air and alkali.

I in-



I introduced some iron filings, recently prepared, into a mixture of about 16 parts of water, and 1 of pale nitrous acid : when they stood some time, phlogisticated air was produced, but not a particle of nitrous air. It may be proper to acquaint my reader, that I guessed the above proportion ; but as a variety of proportions will answer, the experiment cannot fail of success. Here the few particles of the nitrous acid which come in contact with the metal, are wholly deprived of their dephlogisticated air ; and as the phlogisticated air is at too great a distance from the molicules of nitrous acid, and as its attraction is too weak to decompose water, it instantly collects atmospheres of fire, which defend it, in its passage through the solution, from the action of the dephlogisticated air of the suspended acid.

When first I made this experiment, I obtained inflammable air, which puzzled me very much ; but recollecting that I purchased the acid at a common chemist's, I immediately suspected what I afterwards found to be true ; for, on dropping the solution of silver in some of this acid, an immediate

mediate cloudiness succeeded : therefore I was obliged to have recourse to this method of purifying it.

In order to separate the whole of the marine acid from the nitrous acid, without an impregnation of nitrated silver, I would recommend both time and patience. A single drop only of the solution of silver should be used at a time, and the cloudiness of each drop should subside before another is added.

This experiment not only confirms the foregoing explanation of the decomposition of nitre and nitrous acid by metals, but likewise tends strongly to confute the phlogistic theory. Here the metal is calcined, and there is neither inflammable nor nitrous air produced. Let us add to this an experiment already described, viz. the solution of iron in volatile vitriolic acid, without the production of inflammable air ; and the decomposition of this again by nitrous acid, without the extrication of nitrous air or phlogisticated air, though the metal is calcined. Let the phlogistians explain these two last experiments on rational principles in their doctrine, and then I have done ;  
unless

unless they suppose that phlogisticated air itself is a compound of phlogiston and something else; and they might as well say, that the concrete matter of light inflammable air, or of dephlogisticated air, is a compound: besides, there is no phlogisticated air produced by decomposing a solution of iron in volatile vitriolic acid, by the nitrous acid. This experiment may be accounted for in the antiphlogistic doctrine, in the following manner:

The volatile vitriolic acid, as has been already shewn, dissolves the iron, by which it is reduced into its primary particles, and dispersed through the solution. Nitrous acid dropped into this, mixes likewise in the solution; and from the quantity of water which must necessarily be present in volatile vitriolic acid, and in nitrous acid, the ultimate molecules of both substances are removed from one another; whereby only a single primary particle of iron can meet only a single molecule of nitrous acid, which can supply it with both dephlogisticated air of calcination and acid of solution; and thus no nitrous air is produced.

The



The multiplicity of ultimate surfaces, which are as if it were concentrated, or crowded into so small a compass in metals, from the nature of their texture, is the chief cause of the decomposition of nitrous acid during their solution in it; particularly when the pale or colourless nitrous acid is used.

Mr. Lavoisier, to whom we are chiefly indebted for reducing this useful science into a rational system, and expelling that gloom which had overwhelmed it for all ages past, took 945 gr. of nitrous acid, whose specific gravity was 1,316, and to this he added 1104 gr. of mercury\*. The whole of the mercury was dissolved, and he obtained 273,234 cubic inches of nitrous air. He afterward exposed the mercurial salt to a red heat, and obtained from it 287,742 cubic inches of dephlogisticated air, at the same time that the mercury was revived.

Mr. Lavoisier justly drew the following conclusions from the above experiment: 1st, That the weight of the airs produced

\* Mem. Par. 1776, p. 670.

gave the weight of the real acid contained in 945 grains of spirit of nitre, whose specific gravity was 1,316. 2d, That nitrous air was a constituent principle in nitrous acid; and that its production merely depended upon a portion of dephlogisticated air being withdrawn from it, as it formed nitrous acid again on the restoration of its dephlogisticated air. Lastly, That the mercury loses nothing; but that its calcination depended solely upon its union to dephlogisticated air, as it had been revived by the mere expulsion of it again.

Mr. Kirwan objects to these conclusions\*, 1st, Because the whole of the acid could not be decomposed, as a portion must have necessarily passed over during the distillation of the mercurial solution. 2dly, Because it had not been proved by Mr. Lavoisier, that the nitrous air was not produced at the expence of one of the constituent principles of the mercury. 3dly, As the same quantity of nitrous acid had not been produced by the re-union of both airs, and as there had been an excess of one of them.

\* Essay on Phlogiston, p. 63.

I do not see the force of the first of these objections; for what does it avail whether the acid was in part, or wholly decomposed? The only inference that can be drawn from it, is, that the spirit of nitre used contained more real acid than Mr. Lavoisier or Mr. Kirwan himself supposed; or, that the airs contained more water than they imagined, or something else which did not exist in the spirit of nitre, and which of course the metal must impart. But Mr. Kirwan allows, that the airs do not acquire any additional weight from the mercury; for he says \*, "The weight of the acid actually combined with the mercury during the solution, must agree with that of the airs obtained; for, though the phlogiston of the nitrous air was taken from the metal, and therefore foreign to the acid, yet, as the metal was at last revived, it must have taken from the acid as much phlogiston as it gave to it."

Mr. Kirwan's second objection is certainly the only loop-hole left for the phlogistic theory, and for that reason requires

\* Essay on Phlogiston, page 67.



the strictest scrutiny. He supposes, as I have already observed, and as I shall mention here in a few words, that the mercury gives up its phlogiston to the nitrous basis, by which it is converted into nitrous air, at the same time that the fixable air of the nitrous acid unites to the metallic basis and forms a calx. He likewise disposes of another portion of phlogiston, by saying, that it decomposes part of the nitrous basis, and forms fixable air by uniting to its dephlogisticated air. The remainder of the phlogiston, as he supposes, combines both with 19 grains of phlogisticated acid that come over uncombined, and with the compound of acid and calx. After thus distributing the quantity of phlogiston contained in the metal (and indeed he might have contrived to dispose of as much again in the same manner), he supposes that the fixable air is decomposed during the revival of the mercury; and that its phlogiston unites to the metallic basis, at the same time that its dephlogisticated air is expelled in its simple aerial state. But, as the quantity of phlogiston in the fixable air is not equal to the quantity the mercury gives out in order  
to

to become calcined, and of course insufficient to revive the metallic basis, he contrives to have this deficiency supplied by that portion combined with the acid and calx. This is Mr. Kirwan's opinion, and I must confess I do not see how he can justify it. Therefore, convinced that his method of supporting this hypothesis carries with it no sort of conviction, to avoid prolixity, I shall not enter into a detail of it, but refer my reader to the author's own words\*.

Mr. Kirwan's calculating the quantity of phlogiston contained in the ingredients used in the above experiment, does not in the least tend to prove the presence of the smallest quantity of phlogiston, or the matter of light inflammable air. It is a very easy matter to make numbers agree with what never existed but in imagination.

The hypothesis of fixable air being demonstrably erroneous, the phlogistic doctrine appears very defective in the above experiment. The phlogistians must actually acknowledge, that either the metal or the nitrous air contains no phlogiston.

\* Essay on Phlogiston, pages 67-8-9.

If nitrous air were composed of nitrous basis, saturated with phlogiston, how comes it to pass that metals are calcined in it?

Dr. Priestley fused some iron in nitrous air; it calcined and increased in weight, and nothing but phlogisticated air remained\*. Mr. Kirwan explains this experiment by saying, that the dephlogisticated air of the nitrous air unites to both the phlogiston of the metal and to that contained in the nitrous air itself, and forms water, which unites to the metallic basis. Here he supposes a calx to be formed by the union of water to the metal, and in other circumstances by the union of fixable air. Is this consistent? 122 gr. of nitrous air, according to Mr. Kirwan, contain 22 gr. of phlogiston, 66,36 gr. of dephlogisticated air; or, to make a good allowance for it, let us say 68 gr. and the remainder is phlogisticated air. By this, the proportion the dephlogisticated bears to the inflammable air, is nearly as 3 to 1.

According to Mr. Lavoisier, the proportion of dephlogisticated air in water, is to the inflammable air as 7 to 1; and indeed,

\* vi. Pr. 304.



agreeable to all experience, it is at least 6 to 1.

Therefore, laying aside the phlogiston of the metal, after the condensation of the dephlogisticated air into water, we should have a large residuum of inflammable air in the above experiment. Besides, if metals be saturated with phlogiston in their perfect state, they must either part with it on uniting to water, or else, by the joint attraction of it, and the metallic basis, unite with dephlogisticated air simply, and leave the whole of the phlogiston of the nitrous air behind.

The same excellent philosopher reduced nitrous air, by taking the electric spark in it to  $\frac{1}{3}$  of its bulk; nitrous acid was produced, and the residuum was phlogisticated air. At another time he reduced nitrous air to  $\frac{1}{4}$  of its original bulk by the electric spark, and the residuum contained  $\frac{1}{4}$  of nitrous air \*. He likewise, in one experiment, reduced one and a half measure to 0,4 of a measure, by electric explosions taken in a vessel of mercury, with water on the surface of it. The water was acid to the taste, and his iron conductor was partly dissolved.

\* Vol. vi. p. 312.

Mr. Kirwan explains these experiments, by supposing, that the dephlogisticated air unites to the phlogiston of the nitrous air, and forms water ; and that the nitrous acid produced was originally formed and suspended in the air. From what I have already said, it appears, if nitrous air contained phlogiston, we should have a residuum of inflammable air in these experiments, as not containing dephlogisticated air enough (according to Mr. Kirwan's own calculations), at least by  $\frac{1}{4}$ , to convert the whole of the phlogiston into water. July 1787 I repeated the above experiment (with a view different to the present) ; and, after passing the nitrous air in caustic volatile alkali, reduced it by repeatedly taking the electric spark in it to about  $\frac{1}{4}$  of its bulk, nitrous acid was produced, and the residuum was pure phlogisticated air. Having narrowly attended to this experiment, I was at that time induced to suppose, but am now fully convinced, that nitrous acid is formed here in consequence of a decomposition of part of the nitrous air, whereby the remainder is furnished with dephlogisticated air, and so forms nitrous acid, at the same time that

gified

the phlogisticated air of that portion of dephlogisticated air that forms the new compound, remains single and alone. Whenever Dr. Priestley diminished nitrous air by fusing iron in it, no acid (as he observes) was formed. He likewise found, that minium could not be reduced by the heat of his burning lens in nitrous air \*. If the quantity of phlogiston, which Mr. Kirwan supposes, existed in nitrous air, metallic calces should be revived in it; but, on the contrary, metals are calcined in it. This must be very unfavourable to Mr. Kirwan's doctrine; for the supposition that nitrous air retains, as one of its constituent principles, the phlogiston of the metal, is the whole support of his theory; as, by this, he is enabled to say, that the fixable air is decomposed by giving up its phlogiston to the metal, whereby we obtain dephlogisticated air in its simple aerial state. But if the metal should not lose its phlogiston, fixable air cannot by any means be supposed to be decomposed; and of course, if it were one of the constituent parts of

\* Vol. VI. p. II.



nitrous acid, it should be obtained from the calx in its natural state. Indeed, if we compare the quantity of fire disengaged, during the union of dephlogisticated air and light inflammable air, or the heavy inflammable air, or even the solid matter of charcoal, sulphur, and phosphorus, to that developed during the rapid combination of nitrous air and dephlogisticated air, we shall not hesitate a moment to say, that it unites in this latter to a substance quite different from either of the former substances, and that the compound is of a different nature. Dr. Priestley found, that nitrous air, confined above a year in contact with iron standing in water, was reduced, and that the residuum was phlogisticated air\*. I have exposed nitrous air to iron filings and water for three months; it was diminished nearly  $\frac{2}{3}$ , and extinguished a candle.

It is very well known, that iron exposed to water alone will produce inflammable air; then if nitrous air were composed of light inflammable air, dephlogisticated air and phlogisticated air, we should obtain

\* Vol. ii. p. 177.

pure phlogiston, or light inflammable air, in the above experiment.

Is it not contrary to all laws, so far as experience has enabled us to judge, to suppose that iron, if it were saturated with phlogiston, should give it out in contact with water, which is composed of dephlogisticated air and light inflammable air, at the same time that, exposed under the same circumstances to an aerial compound of light inflammable air, dephlogisticated and phlogisticated air, it should absorb an additional quantity of phlogiston? This likewise appears the more extraordinary, when we find that iron, and other metals, unite in the dry way to a sufficiency of dephlogisticated air to saturate them; which shews, if they attract it in consequence of phlogiston, that they contain phlogiston enough of their own, without the assistance of foreign phlogiston. Hence I should suppose, that iron could not influence the phlogiston of nitrous air; or if it should attract it and dephlogisticated air jointly, that it must part with its own phlogiston.

This circumstance alone of metals withdrawing dephlogisticated air from nitrous  
air,

air, and leaving only phlogisticated air behind, proves that either the metal or the nitrous air contains no phlogiston; and indeed, in addition to other adduced facts, it convinces me, that neither contains a particle of the matter of light inflammable air.

It is now very well known, that hepatic air is composed of light inflammable air and sulphur. If equal parts of hepatic air and nitrous air be mixed, they will contract to more than  $\frac{3}{4}$  of their bulk. Sulphur will be precipitated, and the residuum is dephlogisticated nitrous air; which, as shall hereafter appear, contains no such thing as phlogiston. Is it reasonable to suppose, that hepatic gas should take light inflammable air, or phlogiston, from the nitrous air, when it is already saturated with what they call phlogiston? Dr. Priestley likewise reduced nitrous air to more than one half, by exposing Homberg's pyrophorus to it, which had taken fire in it, and the residuum was dephlogisticated nitrous air, and no acid was produced. These facts tend strongly to prove, that nitrous air does not contain the matter of light inflammable



Mr. Kirwan's third and last objection does not appear to me to be of such moment as the former. It is true, as this philosopher observes, there had been an excess of dephlogisticated air produced : I mean by excess, a greater quantity than the nitrous air obtained could condense in the ordinary way of mixing them.

The quantity of nitrous air obtained was 273,234 cubic inches, or 101,09 gr. and the dephlogisticated air amounted to 287,743 cubic inches, or 97,83 gr. The above quantity of pure nitrous air contains 91,78 cubic inches of phlogisticated air, and 182,156 cubic inches of dephlogisticated air, which, in addition to the quantity expelled from the calx, make 469,898 cubic inches of dephlogisticated air ; which, subtracting 14,512 cubic inches from them, make five of dephlogisticated air to one of phlogisticated air, being the exact proportion of perfect nitrous acid.

By these calculations I find, if Mr. Lavoisier used perfect nitrous acid, that the excess of dephlogisticated air is not so great as Mr. Kirwan imagines. Before we attempt to judge of the excess of dephlogisticated

gified air, in the above experiment, the quantity of phlogified air mixed with both the airs should have been first ascertained, by which we might estimate the quantity of nitrous air this would form.

Mr. Kirwan seems to make no allowance for this, though he acknowledges that phlogified air is disengaged, which partly mixes with the nitrous air, and partly unites to the fixable air combined with the calx; which, he says, is partly decomposed during the decomposition of the fixable air by the revivification of the mercury\*. I do not understand what he means by the decomposition of phlogified air, for it has not, to our knowledge, been as yet decomposed. Mr. Kirwan likewise mentions, that during the decomposition of nitre (*per se*) a portion of the phlogified air is decomposed and burned, without any farther information on the subject. If he can decompose this, he certainly will do more than I at present suspect.

Taking the foregoing circumstances into consideration, by what I can infer from Mr.

\* Essay on Phlogiston, p. 69.

Lavoisier's experiment, together with my own observations on the same subject, I think both the combined and uncombined phlogisticated air must be to the dephlogisticated as one to four, which is the portion of the pale nitrous acid. Can this be called an excess? Nitrous air is allowed to contain one of phlogisticated to two of dephlogisticated air: pure nitrous air will readily unite with half its bulk of dephlogisticated air, and form the orange coloured nitrous acid. Every 54 gr. of this acid contain, including the water which the airs hold in solution, 41,665 gr. of dephlogisticated air, and 12,335 gr. of phlogisticated air. Therefore it contains 5 grains in 24 more than the red nitrous vapour does. These proportions differ widely from those of the perfect nitrous acid, which shews, though nitrous air will not readily unite to more air in the ordinary way than the proportion mentioned above, that it will in time condense a larger quantity. Analogous to this is the formation of vitriolic acid; for sulphur will not combine during its combustion with much more dephlogisticated air than is sufficient to convert it into volatile vitriolic acid, but in time, by help of water, heat,



heat, and exposure to air, it absorbs a sufficient quantity to form perfect vitriolic acid.

Red nitrous acid exposed to dephlogisticated air, will gradually absorb it, and in time, if supplied with a sufficient quantity of it, will become colourless. I repeated this experiment to my satisfaction in the year 1786. I do not claim the originality of it; it is to Dr. Priestley we are indebted, as well for this, as for his many other valuable experiments. The same philosopher found, that fuming spirit of nitre, which is not the most perfect, phlogisticates, as he is pleased to call it, common air\*. He likewise observes, that the colourless nitrous vapour will not affect dephlogisticated air, or vitiate common air†. I exposed dephlogisticated air to the perfect nitrous acid for three weeks, and it was not in the least changed. I found, that the red nitrous vapour will diminish common air, but not so readily as the red nitrous acid. Though the perfect nitrous vapour will not diminish dephlogisticated air, yet it has the reverse effect, for it will readily contract nitrous air. This shews that it is fully

\* Vol. II. p. 165.

† Vol. II. p. 165.

saturated

faturated with dephlogisticated air, and is in the state already described. Dr. Priestley found, that melted nitre absorbs dephlogisticated air \*. A solution of nitre, which had been melted, likewise absorbed dephlogisticated air. I have shewn, that nitre and vitriolic acid, heated together, absorb dephlogisticated air, whereby we obtain the most perfect nitrous acid. Hence it is evident we are not rashly to conclude, that, because dephlogisticated and nitrous air will only unite in certain proportion, the compound will not take in more dephlogisticated air under more favourable circumstances. These are my reasons for differing from Mr. Kirwan, in his objections to Mr. Lavoisier's conclusions respecting the decomposition of nitrous acid by mercury.

As mostly all animal and vegetable substances, which have an affinity to pure air, decompose nitrous acid on the same principle with the metals, I shall pass them over in silence, except the two following. Charcoal does not decompose nitrous acid, even by help of digestion; the acid may

\* Vol. II. p. 165.

be expelled from it in whitish fumes. It is extraordinary, if nitrous air be produced in consequence of phlogiston, that it is not obtained in the above process; for the basis of nitrous air will take phlogiston from the metals, and the metals will take it from charcoal; which proves, that metals, if they do contain phlogiston, hold it with greater force than charcoal. In short, almost the whole of charcoal is phlogiston, if such we may call a substance which will wholly unite to dephlogisticated air, or, in other words, burn.

It is true it may be said, that the attraction of the metallic basis to the fixable air of the nitrous acid, enables the nitrous basis, by virtue of a double affinity, to combine with its phlogiston during the solution; and that there is nothing in charcoal to attract the fixable air. In answer to this, I would observe, that the production of nitrous air by oils and spirits of wine and turpentine, contradicts such an hypothesis; for they contain nothing to attract fixable air, and they even produce uncombined fixable air, which strongly proves, if nitrous air contains phlogiston, that it can expel fixable



able air from its basis, in consequence of its superior affinity to it.

I have already shewn the difficulty of uniting charcoal to dephlogisticated air, notwithstanding their strong affinity to each other; and that this proceeds from the aggregate attraction of charcoal. I have likewise observed the necessity of applying heat sufficient to overcome this attraction, in order to combine charcoal with dephlogisticated air; and I think this is the most reasonable mode of accounting for the above experiment.

The carbonaceous matter is held in chemical solution, in oils and spirit of wine, by light inflammable air, water, and a small quantity of fixable air; therefore two substances contribute to the decomposition of nitrous acid in oils and spirit of wine, by which we obtain fixable air, phlogisticated air, and nitrous air, at the same time that water is likewise formed.

Mr. Proust found, that strong nitrous acid will set fire to charcoal, if it be rendered very dry\*. He likewise remarked, that charcoal exposed a few hours to the

\* Tourn. de Medicine, 1778.

air, after calcination, was unfit for the experiment. Charcoal, as Mr. Proust well observes, attracts moisture very forcibly. Therefore, the first effect of the charcoal on the nitrous acid, is to withdraw a portion of its water from it, by which it is rendered highly concentrated, at the same time that the condensation of the water heats the charcoal in a small degree, but sufficiently to volatilize a nitrous vapour; which as soon as it reaches that portion of dry charcoal next the humid part, is condensed by it, and generates heat enough to promote the decomposition of the nitrous acid. Hence we find, why the experiment will not succeed if the acid be poured on the surface of the charcoal.

The effect of nitrous acid on blood is very singular; and though it has not much to do with what we are upon at present, yet, hoping that any fact relating to so interesting a subject may be acceptable to my reader, I shall give as brief an account of it as I can.

Two parts of blood procured fresh at the butcher's, one of strong nitrous acid, and about  $\frac{1}{5}$  of the whole of water, were digested

gested in the heat nearly of boiling water (fresh portions of water being occasionally added), until the whole of the acid was expelled, when it acquired nearly the colour, and exactly the taste, of bile. When mixed with a large quantity of water, it acquired a fine yellow colour; and, on standing, deposited a substance of a brighter yellow, though the supernatant liquor still retained a yellow colour, and bitter taste, but not so intensely as when the precipitate was suspended in it.

The different stages of this process were well worthy of observation. No nitrous air was produced, and the acid was expelled in the state of a white vapour. I tasted the liquor at different periods of the process, and was highly pleased at the gradual progress of the bitterness in proportion as the acidity vanished. About the middle of the process the solution first tasted acid, but was quickly succeeded by a bitter sensation. It appears to me that the nitrous acid took dephlogisticated air from the blood; for though I used the red nitrous acid, it was expelled in a perfect state. At this time I had not leisure to make any farther in-



quiries into this subject, being busy in assisting at a public course of chemistry, at Oxford; nor have I had since an opportunity of enjoying the pleasure I then promised myself in so interesting an investigation.

I think a series of experiments made on this subject, could not fail of being productive of some benefit to mankind. For how can chemistry be better applied than in those investigations, which may tend to throw light on the different disorders incident to man?

Dr. Priestley has discovered a species of nitrous air which supports combustion, destroys animal life, and is condensable in water. This he has called dephlogisticated nitrous air. I consider dephlogisticated nitrous air to be the last stage of nitrous acid, and to be less understood than the four preceding. I exposed four equal quantities of nitrous air in different tubes, to a nearly equal proportion of iron and water. In three weeks the air was diminished  $\frac{1}{6}$ , and the residuum extinguished a candle, and reduced common air. In three weeks more it was reduced about  $\frac{1}{4}$ , and the residuum suffered a candle to burn in it faintly. When it stood a  
fort-

fortnight longer, the diminution was nearly  $\frac{1}{3}$  of its bulk, and a candle burned in the residuum with an enlarged flame. I let the other tube stand until the air contracted to more than  $\frac{1}{3}$  of its original bulk; the residuum was phlogisticated air, and had the smell of volatile alkali. From the progress of these experiments, I did not hesitate to conclude, but that which is called dephlogisticated nitrous air, is common nitrous air, deprived only of a portion of its dephlogisticated air. Dr. Priestley found that nitrous air, which stood in contact with iron and water for four months, extinguished a candle\*. He likewise found that a candle burned with an enlarged flame in nitrous air which had been in contact with iron, over mercury, about six months. The same philosopher found that nitrous air exposed to liver of sulphur for a day was diminished  $\frac{1}{3}$  of its bulk; a candle burned in the remainder with an enlarged flame, and it was not in the least diminished by nitrous air†. I have frequently observed that nitrous air, when reduced to

\* Vol. II. p. 177.      † Vol. II. p. 178.

$\frac{2}{3}$  of its bulk, always admitted a candle to burn in it with an enlarged flame; but that in proportion as it got below this standard, it supported flame so much the worse, until it was reduced nearly to  $\frac{1}{3}$ , when it extinguished a candle.

These facts leave no room to doubt, but that dephlogisticated nitrous air contains less dephlogisticated air than the common nitrous air.

Dr. Priestley found that clean small needles exposed to nitrous air, confined in dry mercury, did not in the least diminish it, though they had stood six or eight months in the same state. But when he introduced a few drops of water, the air was diminished in a few days, and continued so to do until  $\frac{1}{3}$  disappeared, and the residuum was dephlogisticated nitrous air \*. He likewise found that a quantity of nitrous air which had been exposed nine months to iron filings, over mercury, was diminished  $\frac{1}{2}$ , and a candle burned in the remainder, better than in common air, though a mouse died in it. These two experiments shew

\* Vol. VI. p. 316.



that moisture promotes the decomposition of nitrous air. For, 1st, when the materials were perfectly dry, no sensible change took place in the nitrous air. 2dly, When water was added, the absorption took place very soon. 3dly, When less moisture was used, the decomposition went on very slow. Hence it appears that the water is decomposed, and that its dephlogisticated air unites to the metal, at the same time that the dephlogisticated air of the nitrous air combines with the inflammable air, at the very instant of its liberation, and regenerates water. I have already rather conjectured on what principle this last union takes place.

It is very well known that iron, when exposed to a very dry atmosphere, does not rust; and likewise that iron confined in water will yield inflammable air, though it will produce no inflammable air when advantageously exposed both to water and dephlogisticated air. Thus iron filings and sulphur wetted with water, and exposed to dephlogisticated air, will yield little or no inflammable air, until the whole of the dephlogisticated part is nearly ab-

forbed, and then inflammable air is produced in abundance. Dr. Priestley resolved dephlogisticated nitrous air into its constituent principles, viz. phlogisticated and dephlogisticated airs, by heating bits of dry crucibles in it \*. He likewise rendered this air wholly immiscible with water, by passing the electric spark in it, and it was of the standard of 1,45. I repeated this experiment with a view to the presence of fixable air, and inflammable air, but I could not detect a particle of either. It is evident from the correspondence of these facts, that nitrous air and the dephlogisticated nitrous air are composed only of two principles, namely, phlogisticated and dephlogisticated air, and that they only differ in the proportion of these; and likewise that neither contains a particle of light inflammable air, or fixable air.

It is the opinion most generally received from the formation of volatile alkali, during the diminution of nitrous air, by iron and water, that the property of dephlogisticated nitrous air proceeds from a condensation of a portion of its phlogisti-

\* Vol. VI. p. 332.

gated air. I was inclined to this myself; but when I considered the greater number of surfaces which the dephlogisticated air must expose to the iron, than the phlogisticated, being in the proportion of two to one; together with the greater affinity of dephlogisticated air to inflammable air than the phlogisticated, I began to be in suspense. It is true, a portion of phlogisticated air is condensed, but the quantity is trifling in comparison to that of the dephlogisticated air; for generally  $\frac{1}{3}$  of the bulk of a quantity of nitrous air is left unabsorbed, which is nearly the whole of its phlogisticated air. There is no volatile alkali formed during the combustion of Homberg's pyrophorus in nitrous air, for it contains nothing to condense phlogisticated air, and yet the residuary air after the combustion is dephlogisticated nitrous air. The same may be observed with respect to the contraction of nitrous air, by liver of sulphur: it can neither withdraw phlogisticated air nor light inflammable air from it, and yet there is a residuum of dephlogisticated nitrous air obtained, when the air is diminished  $\frac{1}{3}$ . The progress



progress of this last experiment may attest the truth of what I say.

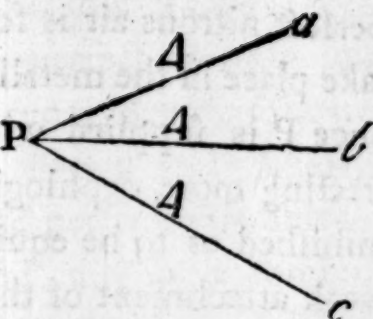
Indeed the method of procuring dephlogisticated nitrous air, by the solution of metals in nitrous acid, favours the foregoing notions; for we can never obtain dephlogisticated nitrous air from nitrous acid, until it is nearly saturated with a metal; and then by introducing more of the same metal, or a different metal, we obtain dephlogisticated nitrous air.

In order to understand this, we must first consider, that the nitrous acid which holds the metallic calx in solution, is in the state of red nitrous acid; or rather more imperfect. Therefore, though the metal deprives the acid of solution in contact with it, of the whole of its dephlogisticated air, yet the particles of phlogisticated air recover a portion of it again from their neighbouring particles of acid, on principles which I have already endeavoured to explain.

To render this the more perspicuous, let us suppose the acid of solution to be

P a

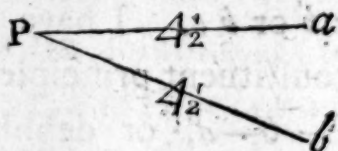
$Pabc$ . Let  $abc$  be its portion of dephlogisticated air,  $P$  combined with the annexed forces; if a metal be introduced into such solution, it will deprive  $P$  of  $abc$ ; then  $P$  being in contact with another particle of acid of solution, will instantly deprive it of either  $a$  or  $b$  or  $c$ . I should suppose, from what has already been said on this subject, that it would be superfluous to explain here, why  $P$  cannot unite to  $ab$  or  $bc$ . I have shewn above, that the constituent principles of the new compound  $P-6-a$ , or dephlogisticated nitrous air, are united with the force of 6.



It may at first sight appear, that a metal introduced into the red nitrous acid in its simple state, should on this principle produce dephlogisticated nitrous air. But be it considered, that though a particle of phlogisticated air can only take one particle of dephlogisticated air from a single molecule of acid; yet that another molecule in its vicinity will supply it with another particle of dephlogisticated air, by which  
perfect

perfect nitrous air is formed. This cannot take place in the metallic solution; for when once P is supplied with  $a$ , its power of attracting more dephlogisticated air is so diminished as to be equipoised, even by the weak attachment of the acid of solution to its suspended metal.

Having thus endeavoured to explain the nature of perfect and imperfect nitrous airs, for such I shall for the future take the liberty of calling them; we can readily account to a degree of certainty, why these do not affect each other when mixed. Let  $p-b-a$  be imperfect nitrous air, and  $P-a$  perfect nitrous air;



if these be mixed,  $P-a$  cannot take  $a$  or  $b$  from P, for P retains them both with as great force as  $P-a$  can attract either. Why this species of air is more soluble in water than the perfect nitrous air, is what I cannot account for, unless it be from the smallness of its atmospheres of fire, which admit the molecule of air to come within the gravitating influence of the water. It is rather remarkable, that  
the



the imperfect nitrous air should favour combustion, when the perfect nitrous air, though it contains more dephlogisticated air, has the reverse effect. It is likewise very singular, that the perfect will unite to more dephlogisticated air in a common temperature, and that the imperfect will not, though it has greater attraction to dephlogisticated air than the former.

That the red nitrous vapour, which contains much more dephlogisticated air, with less force than the two former, should not favour combustion, is still more singular. Again, why Homberg's pyrophorus, as has been observed by Dr. Priestley, will burn in perfect nitrous air, and not in the imperfect, is difficult to be accounted for; unless it proceeds from a better supply of moisture by the one, than by the other.

As these facts cannot be satisfactorily accounted for, I think it better to suspend my opinion, than to attempt plausible explanations, which are generally more productive of evil than good, and only serve as so many allurements to decoy us out of the right path.

If we consider that neither light nor

heavy inflammable air, nor dephlogisticated air, will unite to phlogisticated air, notwithstanding their attraction to it, without the aid of fire, either the electric or a common spark ; and compare this to the easy union of dephlogisticated air and nitrous air, though the latter attracts dephlogisticated air with less force than the three former ; we cannot help attributing it to something that surrounds their gravitating particles, and this we must suppose to be partly fire, as it is disengaged during their condensation. But why fire should not exert this power when nitrous air and dephlogisticated air are brought in contact, is very extraordinary ; more especially when we know, as I have already demonstrated, that their atmospheres of fire must be nearly thrice deeper than those of phlogisticated air ; and likewise when we have every reason to suppose that nitrous air contains nearly the quantity of fire which the dephlogisticated and phlogisticated airs contained in their simple state. It is true, fire is not developed during the union of these last two fluids, which may favour their combination. But how do their  
their

their extensive atmospheres so blend as to bring their gravitating particles within each other's influence?

The condensation of dephlogisticated air, by perfect nitrous air, without the seclusion of fire, is certainly a very striking fact\*.

That nitrous acid contains nearly as much fire as its constituent principles contained before their union, can hardly be doubted; and that it parts with very little of this by its union to an alkali, is also as true as it is singular. Here then nitre contains, in a solid state, fire sufficient to give elasticity to at least 100 times its bulk of dephlogisticated air.

Hence arise the deflagration of nitre and charcoal in close vessels, and the quantity of fire disengaged, though fixable air is produced at the same time.

These facts convince us, that fire unites chemically to bodies, and of course must gravitate towards them. Can we therefore doubt but that fire is a substance, and not a quality, as some philosophers are pleased to suppose?

\* There is heat generated, but not more than should be expected from the re-action of the new formed acid upon the suspended water.

Although



Although the constituent principles of nitrous acid are known, and though they have been united by art, yet we do not well know how nature performs this operation.

Some philosophers, but Mr. Thouvenel in particular, have found that putrefaction favours the production of nitrous acid. All animal substances, during their decay, give out a vast quantity of phlogisticated air; therefore, if dephlogisticated air be present, it will unite to the phlogisticated air in its nascent state, and before it unites with fire. However, I have had an opportunity of observing, that nitrous acid may be copiously generated, where no putrid processes are carried on. The chemical laboratory at Oxford is near six feet lower than the surface of the earth. The walls are constructed with common lime stone, and arched over with the same; the floor is also paved with stone. It is a large room, and very lofty. There are separate rooms for the chemical preparations, so that nothing is kept in the laboratory, but the necessary implements for conducting experiments. There is an area adjoining it on a level with the floor, which, though not very large, is sufficient

sufficient to admit a free circulation of air. The ashes and sweepings of the elaboratory are deposited in it. There is a good sink in the centre of this area, so that no stagnated water can lodge there. The p——y, which is seldom frequented, is over ground, and unconnected with the elaboratory. Notwithstanding all this, the walls of the room afford fresh crops of nitre every three or four months.

Dr. Wall, who paid particular attention to this circumstance, and who told me it contained fixed vegetable alkali, requested I would analyze it, and let him know what proportion of it a quantity would yield. Accordingly I did, and found that two ounces of it contained six drachms of nitrated fixed vegetable alkali, and three of calcareous nitre. The nitre first appears in small whitish filaments, as fine as cob-web, which, when they get a little larger, drop off, so that they never acquire growth sufficient to distinguish their figure to a naked eye. On finding that they contained fixed vegetable alkali, I concluded that it proceeded from minute vegetation; but in this I was mistaken; for I found that they were soluble in

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water,

water, and that they detonated with charcoal at every stage of their growth. Having swept this saline efflorescence from the wall, I dug deep into it, but could not obtain nitre from it. When a part had been white-washed, it yielded nitre, but not so abundantly as a neighbouring spot which had not been treated in the same manner. Hence it is evident, that nitrous acid may be formed without the assistance of putrescent processes, in a still damp air, where there is a substance to attract it when half formed, whereby it is in time brought to perfection. The above facts moreover prove, that fixed vegetable alkali is a compound. Thus we find that chemistry is still in its infancy, and that there is a great deal to be done in order to bring it to perfection.



## SECTION V.

*Of the Marine Acid.*

**T**HE basis of marine acid has not as yet been discovered; but that dephlogisticated air is one of the constituent principles of this acid is very evident, if it enters into the constitution of the nitrous or vitriolic acid.

Charcoal, sulphur, *light* inflammable air, or phosphorus, cannot take its dephlogisticated air from the marine basis, whether the acid be combined, or in its simple state.

Lead will take the acid from the fixed alkalies without decomposing it, as will likewise iron when exposed to a damp air for a considerable time, as the celebrated Scheel has observed. I mixed common salt and manganese in various proportions, and exposed them in a reverberating furnace in a well closed crucible for three hours, to heat nearly sufficient to melt cast iron. I treated manganese, salt, and charcoal, in

the same manner, but with no effect. I mixed clay, salt, and charcoal, and salt and clay alone, with very little success. I treated calcined bones, salt, and charcoal, and calcined bones and salt, and likewise lime and salt, in like manner, without effecting any apparent change in the salt.

I have been informed by a Mr. Robertson, an apothecary in Bishopsgate-street, who has made several attempts to decompose common salt, that he partially alkalized it, by exposing it and clay to a fierce heat; but, soon after it got into contact with air, that it became neutral again. It is certain, that salt loses a portion of its dephlogisticated air very readily, as may be seen by its property of accelerating combustion when thrown on the fire. If common salt and litharge be fused, it is in part decomposed; the acid suffers no decomposition, but unites to the lead; whereby it acquires, when the saline matter is washed away, a yellow colour. It is evident from these facts, that the basis of marine acid is a combustible body, and quite different from light inflammable air, charcoal, or any known inflammable substance; and that it attracts dephlogisticated

phlogisticated air with greater force than any substance hitherto discovered. Though charcoal will decompose all other acids (except a few), when united to bodies which will fix them until they acquire a sufficient degree of heat, yet it has no effect on marine acid. In my opinion, metals decompose marine acid during their solution in it, though iron will condense marine air without decomposing it.

Mr. Kirwan is of opinion, that the marine acid consists of a particular basis united to phlogiston, and a certain proportion of fixable air; and that when the marine basis is deprived of its phlogiston, its affinity to fixed air becomes much stronger, whereby it unites to a large portion of it\*. Though I have attentively perused Mr. Kirwan's Fifth Section on Phlogiston, wherein he treats of marine acid, I must confess I could not make out on what grounds he founded this hypothesis. However, before I presume to offer my opinion decisively upon it, I shall minutely inquire into it. Therefore, let us first suppose iron to be

\* Essay on Phlogiston, p. 74.



composed of a certain basis, and phlogiston, intimately combined. Let us also suppose marine acid to consist of a peculiar basis, and phlogiston, intimately united to fixable air, and that this basis attracts fixable air with greater force than it does phlogiston. This granted, when these are brought in contact, what is likely to take place, according to well known chemical laws? for, in matters of ambiguity, we are justified in reasoning from analogy, more especially when it is an established fact, that the decomposition and composition of all bodies, whether they prevail by virtue of a single or double affinity, are regulated by the same power, though variously modified. The acid most undoubtedly cannot be decomposed, as the attraction of its basis to fixable air on the one side, together with the attraction of the metallic basis for its own phlogiston on the other side, are sufficient to prevent it; for, as the inflammable matter or phlogiston of the metal is expelled in its aëriform state, a double affinity does not prevail in the operation, laying aside the agency of fire,

which

which does not much interfere with the present subject.

Hence it appears that the acid, without suffering a decomposition, unites to the metallic basis, and expels its phlogiston; which is Mr. Kirwan's opinion. In this case, pure fixed alkali, or lime, should precipitate the metallic basis in its purity, and thereby enable us to obtain that substance, which occasions such a contest amongst philosophers.

I saturated half an ounce of marine acid with clean iron nails, first having ascertained the quantity of pure fixed alkali necessary to saturate so much acid in its simple state, and found that the solution required the same quantity of alkali to precipitate the whole of the iron; nor did I find any difference in both salts, when evaporated to dryness. Therefore the acid was not in the least decomposed, though the metal was calcined, and its phlogiston disengaged. Whence did it receive its dephlogisticated air; or, according to Mr. Kirwan, its fixable air? The phlogistians have but one mode of answering this, which is, that the metallic basis unites to water. If metallic

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substances

substances were calcined, as Mr. Kirwan himself observes, and as I had an occasion to mention in treating of vitriolic acid, in consequence of water alone, it should not remain so inert when metals are introduced into it, in a common temperature, when iron is calcined by marine acid in the same temperature very rapidly.

If metallic calces, precipitated by pure alkali from the different acids, owed their additional weight and colour to an union with water; a given weight of iron, calcined in the different acids, should be precipitated by the same pure fixed alkali of the same weight and colour. I observed that the precipitates of 20 gr. of iron from the vitriolic, the marine, and the nitrous acid, dried and treated exactly in the same manner, varied in their weights; that from the nitrous being the heaviest, and the marine precipitate next to it again: they likewise differed in colour, which shews their different degrees of calcination. To make this experiment accurately, the precipitates should be well washed with hot distilled water, and by no means exposed to

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the air while they are drying ; for they change colour in a few minutes by absorbing both fixable and dephlogisticated air from the atmosphere. The precipitate of iron attracts fixable air in small proportions, with as great avidity as the alkalies, and I suspect with as great force as pure lime ; but this fixable air may be expelled again from it by a strong heat, without being decomposed. Hence I am induced to suppose, that fixable air is never decomposed during the reduction of mercury by heat. Why are the precipitates from the different acids of unequal degrees of calcination, if water be the calcining substance, if the acids do not impart something to them, more especially when they are equally well supplied with water ? That the acids take an active part in the solution of metals, cannot be denied ; for it is very well known that water will not dissolve them, and that it will not even in any length of time rust gold, silver, platina, or mercury ; though they are soluble in different acids. Then I ask, How the marine acid acts, when iron is introduced into it ? Whether the acid or water divides it into its ultimate particles, and

and expels its phlogiston; or whether they do this jointly; or whether the acid, by its solvent power, only dissolves what the water calcines and deprives of phlogiston, by which it may enable the water to attack fresh surfaces?

This last is certainly the most plausible phlogistic hypothesis in favour of the doctrine of water; although it may with equal plausibility be said, that the marine acid alone unites to the metallic basis, dissolves it, and expels its phlogiston; and when the acid is withdrawn from it by lime or alkalis being in its extreme division, that it instantly rushes into union with water, and forms a calx. Allowing the phlogistians all this, which is the most that can be urged in their favour; there is one circumstance which, I think, if strictly inquired into, will be found sufficient to overthrow it; namely, the precipitation of metals by each other in their metallic state.

In order to know the full force of what I am going to observe, it will be necessary, first, to consider, that if calcination depends upon the union of water, and the expulsion of phlogiston, the metallic basis must  
have

have greater attraction to water than it has to phlogiston; as evidently appears from the calcination of metals by steam. Therefore, on this principle, a metal could never precipitate another metal in its metallic state, from a very dilute solution of marine acid, or of any other acid. For if water, agreeably to the first phlogistic hypothesis, should calcine the metal, while the marine acid dissolved it, how could iron, though it unites to the acid, precipitate copper in its metallic state? Considering that it is surrounded with uncombined water, is it likely that it would influence the water attached to the metallic basis in any degree?

Then all that can be said with the smallest appearance of plausibility is, that the disengaged phlogiston of the precipitating metal expels its water, and unites to the basis. This I think needs no contradiction. The second and last hypothesis that I considered most favourable to the phlogistic doctrine, is that of the water uniting to the metallic basis, the instant the alkali deprives it of its acid of solution. In this case, all the phenomena may be accounted for thus, viz. that the precipitating  
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metal takes the acid from the precipitated, at the same time that it imparts phlogiston to it, whereby it is reduced. This most undoubtedly, losing sight of all analogical reasoning, seems very plausible, and may appear, to superficial inquirers into this subject, very satisfactory. I must own I should be thoroughly convinced of the truth of it myself, were it not for the following considerations: 1st, The easy expulsion of inflammable air from metals by water; which shews, if this comes from the metals, the greater affinity of their bases to water than to phlogiston. 2dly, The ultimate division of the precipitated metal, which favours calcination. 3dly, The presence of such an abundance of water, which they consider to be the calcining substance.

Thus far I have impartially inquired, on the phlogistic principle, into the nature of marine acid by its effects, as we cannot obtain its constituent parts separately; and though I am not much pleased with it yet, I leave my reader to judge for himself.

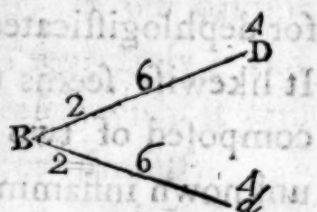
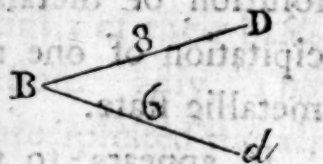
Let us now trace the same subject so far in the antiphlogistic doctrine, and without prejudice compare them to each other.

But

But before we proceed on this, I would have my reader not to lose sight of the following facts, which have already been particularised: 1st, The separation of the marine acid from the metallic solution in its perfect state. 2dly, The precipitation of the metal in a calciform state. 3dly, The active part acids take in the calcination of metals. 4thly, The inconsistency of supposing that the calces of metals are composed of water and a metallic basis. 5thly, The separation of inflammable air, during the solution of metals. And lastly, the precipitation of one metal by another in its metallic state.

It appears to me, and indeed I have no other rational mode of accounting for it, that the acid is first decomposed, and that its basis instantly decomposes the water, and liberates inflammable air; although I think the marine basis has greater attraction for dephlogisticated air than the metals have. It likewise seems to me, that marine acid is composed of two principles only, viz. an unknown inflammable basis, and dephlogisticated air, intimately combined. It may appear rather strange at first sight, that metals

tals should deprive this basis of its dephlogisticated air, notwithstanding their weaker attraction to it. However, I think this may be very well accounted for on the following principles: Let B be the basis of marine acid, D dephlogisticated air; and let these attract each other with the force of 8; and let this be the utmost sum of their joint forces. Let B be possessed of one half of this force, and D of the other half. In this state, metals which I have supposed to attract dephlogisticated air with only the force of 7, could not deprive B of D. Let B, in order to form common marine acid, be united to another particle of dephlogisticated air *d*. They will only unite with the force of 6; that is, the whole force of B will be divided between D and *d*, on principles which I have already explained, in treating of the vitriolic and nitrous acid. Therefore B will retain its dephlogisticated air with only the force of 6; for B can only gravitate with the force of 2 towards D, although D gravitates





vitates with the force of 4 towards B, and  
 for with  $d$  and B. If iron, whose attrac-  
 tion for dephlogisticated air is 7, were  
 brought in contact with the above com-  
 pound in the presence of water, whose con-  
 stituent principles are united with the force  
 of 6, would it not deprive B of both D and  
 $d$ , and would not B instantly re-act on the  
 water, and take from it half the quantity of  
 dephlogisticated air which it before gave up  
 to the metal, and then unite to the calx?  
 Dry marine acid air will unite to iron,  
 without producing inflammable air; which  
 shews that it must come from the water. It  
 is true, it may be said, that the union of ma-  
 rine air to iron, without any separation of  
 its principles, is unfavourable to the hy-  
 pothesis of the decomposition of marine  
 acid, when in contact with water. But be  
 it considered, although the force of 7  
 overcomes the attraction of B to dephlogis-  
 ticated air, that the force of  $\frac{1}{1000}$  is suffi-  
 cient to move it with its dephlogisticated air  
 towards the iron, when there is nothing else  
 to influence it; and we may suppose that  
 the iron itself must attract it with greater  
 force than this. When water is present,

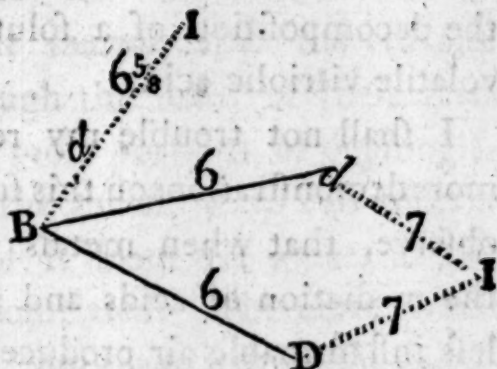
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the case is different: for, when the iron influences the dephlogisticated air of the marine basis with so superior a force as  $3\frac{1}{2}$  to 2; B, or the marine basis, being in contact with water, which retains its dephlogisticated air with the force of  $6\frac{1}{2}$ , or, laying aside reciprocal attraction, with only the force of  $3\frac{1}{2}$ , yields its own dephlogisticated air to the iron, and directs the whole force of its attraction, which is 4, towards the dephlogisticated air of the water; by which it is decomposed, and inflammable is produced. The marine basis being thus furnished with half the quantity of dephlogisticaed air which is necessary to the formation of common marine acid, unites to the calx, and dissolves it. To render this the more intelligible, let I—*d* be a molecule of water,



a molecule of marine acid, and I a surface of iron; let us suppose these to be influenced with the different forces expressed by the numbers annexed to them; is it not reasonable to suppose, as soon as I, or iron, should influence *d* D, that B would re-act on

on  $d$ , or the  
dephlogistica-  
ted air of the  
water, and dis-  
engage I, or B  
inflammable  
air.



I make no doubt but a good mathematician (for I acknowledge my own deficiency) would demonstrate this to a degree of certainty. However, although I am convinced of the truth of it myself, I would have my philosophical reader to strictly inquire into it before he either approves or disapproves of it.

The rest of the antiphlogistians differ from me with respect to the manner in which water is decomposed; for they suppose (if I mistake not) that the marine or vitriolic acid first unites to the metal, and that the compound decomposes the water, from the joint attraction of its constituent principles to dephlogisticated air. If this were true, water, when brought in contact with iron united to marine air, would yield inflammable air, which is not the case; or iron would yield inflammable air with greater rapidity in volatile vitriolic acid, than in perfect vitriolic acid; or marine  
O acid



acid would produce inflammable air during the decomposition of a solution of iron in volatile vitriolic acid.

I shall not trouble my reader with any more demonstrations on this subject, but only observe, that when metals are calcined by the mediation of acids and water, there is less inflammable air produced, by one half, as Dr. Priestley observes, than when they are calcined by steam \*. This is not only explicable on the foregoing principles, but also tends strongly to corroborate them; and, if narrowly inspected, will be found very unfavourable to the phlogistic theory. If the calcination of metals depended solely upon their union to dephlogisticated air, it must be supplied by water, when steam is brought in contact with them; and as every particle of light inflammable air is united but to a single ultimate particle of dephlogisticated air, inflammable air must be disengaged in proportion to the quantity of dephlogisticated air which unites to the metal; or, in other words, according to the degree of calcination it acquires.

\* Vol. VI. p. 102.

But

But this is not the case when metals are calcined in the marine or in the vitriolic acid; for though the bases of these acids impart two or more portions of dephlogistated air to the metal, they can recover but one half of it from the water, as has been fully demonstrated. Therefore, when acids are used, only one half of the quantity of inflammable air should be produced, that is extricated when steam is the calcining menstruum; which could not be the case, if light inflammable air were one of the constituent principles of the metal.

It is true, it may be said, that the metallic precipitate from the above acids corresponds in its degree of calcination with the quantity of inflammable air or phlogiston disengaged, and for that reason retained phlogiston in solution. But I have already shewn, in treating of the vitriolic acid, that the precipitant, whether it be an alkali or an earth, enables the basis of the acid, in quitting the metal, to take from it, its full portion of dephlogistated air, by which the precipitate contains but the portion taken from the water. When the nitrous acid is used, which contains more dephlogistated

air less intimately combined than the marine or vitriolic acid does, the precipitate is found united with more dephlogisticated air; and the nitre obtained by precipitating a neutral solution of nitrated iron by fixed alkali, is far from being so perfect as what may be produced by combining these previous to the above treatment. When iron is introduced into a neutral solution of marine copper, the latter is precipitated in its metallic state, and no inflammable air is produced. This fact, separately considered, appears very favourable to the phlogistic theory. Iron attracts dephlogisticated air with greater force than copper does, although iron alone will not reduce the mere calx of copper diffused in water; but, aided by the basis of marine acid, it will wholly deprive it of its dephlogisticated air. The marine acid, having greater affinity to iron than to copper, quits the latter to unite to the former; and, assisted by the iron itself, it forces with it the dephlogisticated air separated from the water. Thus, by their joint forces, they accomplish what the iron alone could not; and as this quantity of dephlogisticated air is sufficient for the solution



lution of the iron, no decomposition of water takes place, and of course no inflammable air is produced. In short, the dephlogisticated air of the marine acid itself, together with the small portion separated from the water during the solution of the copper (for but little inflammable air is produced), move jointly to unite to the iron, and affect it as dephlogisticated marine acid would, which is known to dissolve metals without generating inflammable air.

Having, as fairly as lay in my power, inquired into the nature of marine acid on the antiphlogistic and the different phlogistic principles, so far as it is affected by metals, I shall now proceed to its other principal properties,

When common marine acid is distilled over red lead or manganese, it undergoes a very great change, as the celebrated Scheel has discovered, in taste, smell, volatility, &c. : distilled or mixed with nitrous acid, it acquires partly the same properties. I doubt whether arterial blood would not effect the same change in it. Marine acid thus treated is said to lose phlogiston, or the matter of light inflammable air: hence

it has got the name of dephlogisticated marine acid.

Some phlogistians attribute this change in marine acid to a loss of its phlogiston, and an union to dephlogisticated air; others, to an union of dephlogisticated air to its phlogiston: but Mr. Kirwan imagines, that it exchanges its phlogiston for fixable air, in order to become what is called dephlogisticated marine acid. Thus the phlogistians themselves differ in opinion; a clear proof of the inconsistency of their doctrine.

The antiphlogistians, on the contrary, are of opinion, that the basis of marine acid, from its great attraction to dephlogisticated air, is capable of uniting to a greater portion of it than it is found combined with in its ordinary state, provided it be presented to it under favourable circumstances.

\* Mr. Kirwan affirms, that he has obtained dephlogisticated marine acid from chalk. Chalk has no sensible attraction to inflammable air; therefore the marine basis must

\* Essay on Phlogiston, page 80.

attract fixable air with greater force than it does phlogiston, for a double affinity does not prevail here. According to Mr. Kirwan, common marine acid must part with phlogiston in order to unite to fixable air; for he supposes, that the marine basis cannot retain both when in the state of dephlogisticated marine acid: then I ask, whether Mr. Kirwan obtained inflammable air in this experiment, or what became of the phlogiston of the marine acid? However, Mr. Kirwan has been more successful than I have been; for I attempted in vain to prepare dephlogisticated marine acid by means of chalk: in short, it had the contrary effect, for it decomposed dephlogisticated marine acid obtained from manganese.

I saturated a quantity of pure volatile alkali with dephlogisticated marine acid carefully prepared; phlogisticated air was produced, but not a particle of fixable air, and the resulting salt was found to be common sal ammoniac. Volatile alkali is composed of light inflammable air and phlogisticated air; therefore it must be partly decomposed, by which phlogisticated air is obtained; and the inflammable air must unite to something



else, which attracts it more forcibly than the phlogisticated air. I ask, to what? Not to the marine basis, for it appears to have already parted with phlogiston to unite to fixable air; therefore it must have greater attraction to it than it has to phlogiston.

Besides, the attraction of the phlogisticated air to light inflammable air, renders such an union very improbable. Or, allowing that the gravitating matter of the light inflammable air united to the marine basis, it must then let go its fixable air in order to become common marine acid; for it cannot hold both, according to Mr. Kirwan himself. Then I ask, what becomes of its fixable air? for I distilled the salt to dryness, and could not obtain it. It cannot be said, that it has been decomposed by the inflammable air of the alkali; for it would be inconsistent to suppose, that phlogiston should influence dephlogisticated air already saturated with phlogiston, and united to another substance.

Equal parts of dephlogisticated marine air and light inflammable air mixed over water, will form, according to Mr. Kirwan \*, a dense white cloud; more than one

\* Essay on Phlogiston, page 80.

half is absorbed, and is found to be common marine acid, and the residuary air is pure inflammable air. Mr. Kirwan considers this experiment as very favourable to his hypothesis, and sufficient to subvert that of the antiphlogistians. In my opinion, if it be narrowly inquired into, it will be found more unfavourable to the former than to the latter doctrine. Therefore, allowing dephlogisticated marine air to be convertible into common marine acid by the mere admixture of light inflammable air: how does the inflammable air act in this case? Does it unite to the basis of marine acid? If so, fixable air (if it were one of the constituent principles of the dephlogisticated marine acid) should be disengaged; but Mr. Kirwan himself has shewn, that not a particle of fixable air is produced. Then all that can be said in favour of the doctrine of fixable air is, that it is decomposed. I should like to know how such a decomposition can take place; for, in order to this, the marine acid basis must exert a certain force on the phlogiston of the fixable air on the one side, while the light inflammable air pulls at its dephlogisticated air on the other, and

so, by their contrary powers, force the constituent principles of fixable air asunder. Is this conformable to the laws of nature, so far as they govern chemical attraction? May not we as well say, that a rope which suspends a weight should first break in the strongest part? Is it not more reasonable to suppose, that the marine basis would the rather unite to the disengaged phlogiston, than struggle for that which is already intimately combined? Even allowing such a decomposition, fixable air should be regenerated; for, according to Mr. Kirwan himself, water has never been formed but in a red heat\*.

The black calx of manganese, free from calcareous earth and iron, will not yield a particle of fixable air by exposure to heat. The acids, even those that will dissolve it, do not expel a particle of fixable air from it. I fused manganese and borax into a vitrescent mass, and yet no fixable air was produced, and little or no dephlogisticated air; but this I do not wonder at, as dephlogisticated air enters into the constitution of

\* Essay on Phlogiston, p. 26.



glafs. If fal ammoniac and manganese be distilled, the fal ammoniac is decomposed, and the volatile alkali is obtained in a caustic state; and the acid is dephlogisticated, as Mr. Kirwan observes. Hence he infers, that the fixable air of the manganese unites to the marine acid; but he should first prove that the manganese contains fixable air. I have distilled caustic volatile alkali and manganese, and yet the alkali was still caustic. Caustic fixed alkali boiled over manganese received no fixed air from it. Lime and manganese treated in the same manner did not shew the smallest vestige of fixable air; and the manganese thus treated, afforded the usual quantity of dephlogisticated air. These circumstances induce me to believe that manganese, when free from calcareous earth, does not contain fixable air in any considerable proportion; and that dephlogisticated marine acid does not contain a particle of fixable air, as one of its constituent principles. In my opinion, the phlogistians must have recourse to some other mode of accounting for the formation of dephlogisticated marine acid, besides that of fixable air; and what

what can this be? They cannot attribute it to the mere separation of phlogiston from the marine acid; for it is evident that dephlogisticated air unites to it, during its distillation with manganese, when we can expel it from the acid again by uniting it to fixed alkali, and when the salt is found to be the same as if the alkali had been combined with common marine acid. Besides, the manganese, after the distillation of marine acid, will yield no dephlogisticated air, although previous to this process it affords it in abundance. Hence it appears, that the phlogistians must allow the presence of dephlogisticated air in the dephlogisticated marine acid; and to support the doctrine of phlogiston, they can only say, that the manganese unites to it at the same time that it imparts dephlogisticated air to the marine acid. If the marine acid parts with phlogiston to unite to dephlogisticated air, how does it recover this again on uniting to fixed vegetable alkali, when its dephlogisticated air is expelled? for it is converted into common marine acid, and, according to the phlogistians, the presence of phlogiston is indispensably necessary to this state. Let us

us now inquire into the nature of dephlogisticated marine acid, and aqua regia, in the antiphlogistic doctrine.

I have already described the nature of marine acid with respect to the attraction of its basis for dephlogisticated air, and the intimacy of their union when in the state of common marine acid. No wonder then that it should unite to more dephlogisticated air, when it meets with it condensed and united with less force than its basis attracts it. A moderate degree of heat will expel dephlogisticated air from red lead and manganese; but the fiercest heat we can produce will not expel the whole of their dephlogisticated air from them. Hence we may infer, that the marine basis may with very little resistance deprive these of a portion of their air, and thereby assume the character of dephlogisticated marine acid. The calces of iron, tin, copper, antimony, &c. will not part with dephlogisticated air in the most intense heat; which shews that they retain it with greater force than the former calces, and of course will not give it up to the marine basis so readily.

I have endeavoured to shew, that dephlogisticated air is retained with less force in  
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the nitrous acid than in the vitriolic acid ; and in the vitriolic, than in the marine acid. I would now observe that, though the marine basis, when united to its natural portion of dephlogisticated air, cannot take this from the vitriolic acid, it will deprive the nitrous acid of a portion of its dephlogisticated air, as holding it with so inferior a force.

Thus, when marine acid is mixed with the nitrous acid, nitrous air is sometimes produced, according to the proportion used. If these two acids be mixed in the proportions of two of the nitrous to three of the marine, provided the acids be strong and complete, and the mixture be kept in a cool place, nitrous air will first be disengaged, attended with heat ; but on standing for some time, and when it gets cool, the nitrous air ceases coming over, and small bubbles of air are generated in different parts of the mixture, which are absorbed almost as soon as they get birth. These sometimes make their first appearance at the bottom of the liquor, and are carried upwards in slender streams, gradually diminishing in their progress, until they can be

be no longer traced, and attended with a hissing noise, occasioned by the absorption. I endeavoured in vain to obtain some of this air. This beautiful appearance does not always take place. A similar phenomenon may be observed in preparing nitrous ether in Dr. Black's method.

Thus we find that the marine acid will take dephlogisticated air from the nitrous, with as much facility as from the calx of manganese, and that it affects this acid as the metals do, by withdrawing dephlogisticated air from it, and not, as the phlogistians imagine, by imparting phlogiston to it; for I flatter myself I have already shewn that nitrous air contains no such thing.

It is very well known that fixable air will not affect nitrous air in the least, and that they cannot be combined by any means whatever. It is likewise very obvious, that nitrous air will not form nitrous acid without the presence of dephlogisticated air. Yet Mr. Pellitier formed nitrous and common marine acid, by mixing dephlogisticated marine air and nitrous air, 26 Roz. 393. This is not only a convincing proof  
of

of the entry of dephlogisticated air, in its simple state, into the constitution of dephlogisticated marine acid, but likewise points out the weakness of the phlogistic theory. For, if nitrous air were disengaged during the action of the marine on the nitrous acid, in consequence of the marine imparting phlogiston to it, and withdrawing from it either dephlogisticated air or fixable air; is it likely that they would decompose each other again, especially when they are in an ærial state, and guarded by fire? Indeed, the phlogistians may urge a similar objection against the antiphlogistic doctrine, by saying that, if the marine acid deprived the nitrous air of its dephlogisticated air, in order to become dephlogisticated marine acid, nitrous air could not deprive it of this again. All this is very fair, and would be difficult to get over, were it not for our minute inquiry into the nature and internal structure of the acids; and likewise the force with which their constituent principles unite, and the manner in which this force must be influenced, according to the proportion of dephlogisticated air united to their bases.

I have



I have already supposed, that the imperfect or dephlogisticated nitrous air is united to its dephlogisticated air with the force of 6; the perfect or common nitrous air with the force of  $4\frac{1}{2}$ ; the red nitrous vapour, or perfect red nitrous acid, with the force of 4; the pale with the force of  $3\frac{1}{2}$ ; and the colourless or perfect nitrous acid with the force of  $3\frac{1}{2}$ . But I would observe that these are often mixed, so that it is a difficult matter to obtain them separately, particularly the red and pale, for the colourless cannot exist in contact with the red. I have likewise supposed that the marine basis, though it attracts dephlogisticated air with the force of 8, is only attached in its common state to its dephlogisticated air with the force of 6; and that it has a tendency to unite to more dephlogisticated air when it meets with it combined with a force inferior to its own attraction to it.

From this statement of the force of union of the constituent principles of common marine acid, and its tendency to unite to more dephlogisticated air, we may suppose that its basis attracts the quantity necessary

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to its dephlogisticated state with the force of 4.

Thus stating the comparative attraction of both acids to dephlogisticated air, rather than their absolute forces, which I think are impossible to be ascertained, we shall be the better able to account for the following facts. Mr. Pellitier has observed, if the nitrous acid be added in small proportion to the marine acid, that it is wholly decomposed, and that its phlogisticated air is disengaged, notwithstanding phlogisticated air attracts the quantity of dephlogisticated air necessary to the formation of perfect nitrous air, with greater force than the marine acid.

This I think is only explicable on the following principles: When a small portion of nitrous acid is diffused in a large quantity of marine, the latter exposes surfaces enough to at once separate the whole of its dephlogisticated air from the phlogisticated. For the force of 4 is sufficient to overcome, if the perfect nitrous acid be used, the force of  $3\frac{3}{4}$ , or if the pale  $3\frac{3}{4}$ ; but if the red nitrous acid be used in its purity, it will not be decomposed, for it retains its dephlogisti-

cated air with as great force as the marine acid attracts it ; therefore they will partially unite without a decomposition.

I have already observed the nature of the above decomposition of nitrous acid, in treating of the effects of metals on it when highly diluted.

When a larger quantity of nitrous acid is mixed with the marine acid, nitrous air is produced ; for, as a molecule of the marine can only deprive a single molecule of nitrous acid at most but of two ultimate particles of dephlogistified air, there are not a sufficient number of the former in contact with the latter to effect a total decomposition ; and as it cannot take place but by a number of uniform pulls from different quarters at once, while the nitrous molecule is perfect, the nitrous air, retaining its small portion of dephlogistified air with greater force than when united to a larger quantity, passes off unmolested in its aerial state in the marine acid.

Thus it is that nitrous air is disengaged by the marine acid, though the nitrous air will take its dephlogistified air from dephlogistified marine air.



I think the dephlogisticated marine air retains its dephlogisticated air with nearly as great force as the nitrous air attracts it; for when the airs are perfectly dry, and mixed over mercury, no decomposition seems to take place until water is introduced. Hence I infer, that water assists in the decomposition from its attraction to marine acid. If a small quantity of marine acid be mixed with a large portion of perfect nitrous acid, no nitrous air is produced, and no change appears in the acid. If more be added, the acid changes colour; but if a larger quantity be added, nitrous air is produced, but no phlogisticated air. This confirms the above demonstration of the total decomposition of nitrous acid; for we find a correspondence in reversing the proportion of the acids.

If marine ammoniac be mixed with the nitrous acid in the temperature of  $70^{\circ}$  or  $80^{\circ}$ , a violent action takes place, and a large quantity of nitrous air is extricated, mixed with a small portion of dephlogisticated marine air and phlogisticated air. Here the marine ammoniac is decomposed; for the nitrous acid, from its superior attraction  
to

volatile alkali, takes it from the marine acid. The marine acid in its turn takes dephlogisticated air from the remainder of the nitrous acid, and forms aqua regia, or dephlogisticated marine acid; a portion of this dephlogisticated marine acid re-acts on the newly formed nitrous ammoniac, withdraws from it its inflammable air, and converts it into water, by supplying it with dephlogisticated air, at the same time that its phlogisticated air is disengaged. This accounts for the greater production of nitrous air when we use marine ammoniac, than when the quantity of marine acid which it contains is used. If the regulus of antimony in fine powder be exposed to the air disengaged during the action of nitrous acid on marine ammoniac, it is instantly calcined, and sparks of fire are emitted. This beautiful appearance will not take place, if the regulus be exposed to the dephlogisticated marine air alone; so that it requires the presence of nitrous air. This is very unfavourable to the phlogistic doctrine; for, if the nitrous air be already saturated with phlogiston, how can it contribute to the rapid calcination of the

antimony? Or, if it should take place in consequence of the attraction of the marine acid to phlogiston, the metal must retain it with less force than the nitrous air. But if this should depend on the attraction of the metallic basis for fixable air, at the same time that the dephlogisticated basis attracts its phlogiston, and so by a double affinity promote the calcination or decomposition, it should take place in pure dephlogisticated marine air. It cannot be attributed to water; for steam in its rarest state cannot produce it, nor will steam and nitrous air afford this phenomenon.

It appears to me, that it can only take place at the very instant that the dephlogisticated marine air unites to red nitrous vapour, which is formed by an union of atmospheric air to the nitrous air, extricated with the dephlogisticated marine air; for both acids attached and destitute of water, which would imperceptibly carry off the fire disengaged by the rapid union of dephlogisticated air to the metal, favour calcination more when thus partially condensed, than either would separately in an  
aerial



aërial state, being then too intimately united to fire.

The marine acid will condense red nitrous vapour in consequence of its dephlogisticated air; and provided the proportion be adjusted, little or no nitrous air will be produced. In like manner, red nitrous vapour, or red nitrous acid, from its attraction to dephlogisticated air, will unite to dephlogisticated marine acid, and not a particle of nitrous air will be produced: here the attraction of both acids to dephlogisticated air is nearly equal; therefore they unite without a separation of either of their principles. Hence arises the difference between what is called aqua regia, and dephlogisticated marine acid; for when marine acid is even combined with a sufficiency of dephlogisticated air to form dephlogisticated marine acid, it will influence the nitrous vapour so as to render it impossible to separate them, from their nearly equal degree of volatility. Although the heat generated by the admixture of the marine and perfect nitrous acid, shews the more intimate union of the dephlogisticated air of the nitrous acid to the marine; yet the volatility of the

compound, or the little force with which its molecules gravitate towards each other, accounts for the specific gravity of aqua regia.

Dr. Priestley diminished common air by passing the electric spark in it, in contact with marine acid; and though he continued the operation some time after the contraction took place, the residuum neither increased nor diminished\*. Dephlogisticated marine acid exposed to the solar light will yield dephlogisticated air, 29 Roz. 82. These two facts, not to adduce any more, are sufficient to confirm the antiphlogistic doctrine. When Dr. Priestley took the electric spark in common air, in contact with dephlogisticated marine acid, it was diminished to one half; but I suspect, as some of the phlogisticated air disappeared, that nitrous acid had been formed.

Thus finding that this change in marine acid depends upon its union to dephlogisticated air simply, we can easily account for the calcination of metals in this acid, without the extrication of inflammable air; for though the metal takes this de-

\* Vol. VI. p. 340.

phlogisticated

phlogisticated air from the marine acid, it cannot recover it again from the water; therefore it re-acts on the metallic calx, and dissolves it. From the attraction of common marine acid to dephlogisticated air, it will dissolve the calces even of those metals which it has no power over when in their metallic state, without producing inflammable air. We can explain on the same principle, why dephlogisticated marine acid will not dissolve metallic calces; for the marine basis and the metals being saturated with dephlogisticated air, cannot influence each other until either loses a portion of its air, by which this neutrality or equilibrium is destroyed. The effect of perfect or pale nitrous acid on manganese and other metallic calces confirms this; for, as the immortal Scheel has long since observed, this acid must be deprived of a portion of its dephlogisticated air, before it can dissolve them; and this is done by the addition of any substance which attracts dephlogisticated air, such as sugar, spirit of wine, &c.

The conversion of sulphur into vitriolic acid by dephlogisticated marine acid, is rather



ther against the phlogistic theory, when we consider that this again, when combined with clay, and exposed to heat, will yield dephlogisticated air. This I mention, because Mr. Kirwan urges it against the antiphlogistians. Bergman says, that sulphur is not vitriolated in dephlogisticated marine acid; but, not having repeated the experiment, I must rest in suspense. Several other facts might be adduced in favour of the antiphlogistic doctrine, but in my opinion it is unnecessary to say any more. Indeed I think every single fact in chemistry is in its favour, even those that have been urged in opposition to it. Therefore it appeared unnecessary to select from the general stock of facts, which induced me to adopt such truths as first occurred to me in my demonstrations.

## SECTION

## SECTION VI.

*Of the Calcination of Metals Via Sicca.*

**A**LL the metals, except gold, platina, and silver, are calcined by the joint action of air and fire. That is to say, they are deprived of their metallic brilliancy, assume an earthy appearance, and acquire an additional weight.

Philosophers vary in opinion respecting the nature of the calcination of metals. The antiphlogistians suppose that metals are simple bodies, which unite to dephlogisticated air, and form calces; and that the mere expulsion of it is sufficient to reduce them again to their metallic splendour; and likewise when charcoal is used to reduce the refractory calces, that it imparts nothing to the metal; but that, by its superior attraction to dephlogisticated air, it separates this from it, by which it is revived.

The phlogistians, on the contrary, are of opinion, that metals are composed of two principles,

principles, viz. metallic bases, and phlogiston (or light inflammable air), in a solid state. Although all the phlogistians allow that dephlogisticated air unites to some of the metals during calcination, yet they do not agree with respect to the nature of the union. Some phlogistians suppose that the dephlogisticated air unites to the phlogiston of the metal, and forms water, which combines with the metallic basis, and constitutes the calx. Others are of opinion, that fixable air is sometimes formed. Dr. Priestley thinks that metals, during their calcination in dephlogisticated air, unite to the water suspended in it, at the same time that the gravitating matter, or acidifying principle of the dephlogisticated air, unites to its phlogiston, and forms an acid.

These are the latest received opinions in the phlogistic doctrine respecting the calcination of metals. That metals give out nothing, but take in dephlogisticated air during calcination, appears from Dr. Priestley's and Mr. Lavoisier's experiments; but that this absorption depends on inflammable air (or phlogiston) has not been proved, and, in



my opinion, there have been very little grounds for such an hypothesis.

Allowing metals to be what the phlogistians suppose, is it likely that phlogiston, which must be the same wherever it is, or however combined, should at one time form fixable air, and at another time water; or, according to Dr. Priestley, nitrous acid? The former doctrine is certainly an excellent improvement on the phlogistic theory; for, without it, this could not stand its ground much longer. But although this hypothesis of fixable air may at first seem plausible in calcination in the dry way, yet that advantage is totally lost when acids are used. Fixable air is formed during the calcination of mercury *per se*, according to Mr. Kirwan; so that mercurius calcinatus is a compound of a metallic basis and fixable air, as are likewise all the mercurial calces. The phlogistians may persist in this hypothesis, for, in my opinion, it appears very favourable to them. 1st, Because it is very well known that fixable air is composed of dephlogisticated air and heavy inflammable air, and therefore can be supposed to impart phlogiston during its decomposition.

composition. 2dly, Because a vast quantity of nitrous air is produced during the calcination of mercury in the nitrous acid, which they suppose to be the phlogiston of the metal and nitrous basis intimately combined. 3dly, Because this last supposition of nitrous air could not be admitted but on the doctrine of fixable air, as the nitrated calx is reduced without addition; which, according to the phlogistians, would be impossible, as the nitrous air carried off its own phlogiston, unless it was united with something which could impart phlogiston to it. Hence we find that, laying aside the presence of fixable air, phlogiston must be subverted. As the phlogiston of the mercury is carried off in the nitrous air, according to the phlogistians, and of course no phlogiston left to form fixable air, which is necessary to the calciform state of the mercury, Mr. Kirwan has been pleased to say, that fixable air is one of the constituent principles of nitrous acid itself, and that it unites to the mercurial basis ready formed. I have already given my reasons for refusing my assent to this; and it has appeared that phlogiston, or light inflammable air, does not  
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enter into the constitution of nitrous air ; therefore it is evident, that the doctrine of fixable air is as delusive as any other phlogistic doctrine. Mercury, as that great philosopher Mr. Lavoisier has first observed, unites to a certain portion of dephlogisticated air during its calcination *per se*, and the additional weight of the calx corresponds with the weight of the air absorbed. By the mere application of heat the air is expelled again, and the mercury is revived. Laying aside all prejudices, this most undoubtedly is a strong argument in favour of the anti-phlogistic doctrine, and is to me, together with the facts already adduced, a convincing proof of the truth of it. Mr. Kirwan would explain this process in the following manner, viz. That the phlogiston of the metal unites to the dephlogisticated air, and forms fixable air, which, re-uniting to the metallic basis, constitutes the calx ; but when a greater degree of heat is applied than was necessary to the calcination, that this fixable air is decomposed, by which its dephlogisticated air is disengaged, at the same time that its phlogiston re-unites to the metallic basis. Even losing sight of  
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what has been already adduced on the subject, it appears to me, that this mode of reasoning, if strictly scrutinized, will be found to carry with it self-contradiction. For, in the first place, it shews that phlogiston, or the matter of light inflammable air, has greater affinity to dephlogisticated air than it has to the metallic basis. In the second place, during the revivification, this evidently appears not to be the case. If mercurius calcinatus were composed of three principles, viz. a metallic basis, phlogiston, and dephlogisticated air; and if the two latter were intimately combined from their superior attraction in the state of fixable air, and attached to the metallic basis, is it likely that any degree of heat, but particularly that sufficient to revive mercury, would separate the constituent principles of the fixable air; more especially when they attract each other with greater force than the metallic basis does either? This still appears the more improbable, when we consider the volatility of fixable air and of its constituent principles. Is it not the property of fire to promote the elective attraction of bodies, or else to resolve compounds

pounds into their constituent principles? And is not this established law wholly perverted, if we suppose mercury to contain phlogiston (or the gravitating matter of light inflammable air)?

Indeed, there are some circumstances in which bodies will decompose others of superior attraction, when exposed to heat; as, for instance, phosphoric acid will decompose vitriolated tartar; but this proceeds from the extreme fixity of the alkali and phosphoric acid, and the volatility of vitriolic acid; a circumstance which does not interfere in the reduction or calcination of mercury.

If mercury were a simple body, whose ultimate particles attract dephlogisticated air, but which, from their own influence on each other, cannot unite to it until this is counteracted by heat, we could account for the calcination of mercury, and the decomposition of the calx again when exposed to a stronger heat, on the same principle that copper and zinc, or gold and mercury, or tin and mercury, unite in a low heat, and separate again in a higher degree.

If the calces of mercury contained fixable air, they would yield it during their re-

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duction in light inflammable air ; which is not the case, as appears from Dr. Priestley's experiments. This philosopher heated red precipitate of mercury in contact with light inflammable air, in close vessels, until eight ounce measures were absorbed, and no fixable air was produced, but a small portion of water\*.

Mr. Kirwan would say, that the fixable air is here decomposed, or rather condensed into water ; which hypothesis is founded upon no experiment whatever. For I am persuaded that no chemist can convert all the principles of fixable air into water, or into any other fluid.

If fixable air was decomposed during the reduction of mercurial calces, the same should take place during the revivification of white lead in light inflammable air, which, we know, contains fixable air in great abundance ; but this does not appear to be the case. If fixed air be convertible into water by intense heat, as Mr. Kirwan supposes, fixed vegetable alkali, or barites, should not yield it after they have been exposed to a strong heat for some time ; or the

\* Vol. VI. p. 129.



electric spark would condense it into water, which Dr. Priestley has shewn does not happen; though, as he has observed, a partial decomposition had taken place. I frequently mixed an ascertained quantity of fixable air with a charge of light inflammable and dephlogisticated air; and though I inflamed them by passing a strong electric spark in them, I found no sensible change in the fixable air. From these and many other similar circumstances I am led to believe, if the calces of mercury contained fixable air, that we should obtain it when we supply the metallic basis with pure phlogiston.

It is surprising to me, if metals be composed of so volatile a substance as light inflammable air and fixed bases, that we cannot separate them in the most intense heat. Surely all the metallic bases are not the same. Therefore we should suppose that there might be one or more amongst them all, that would be so little tenacious of their phlogiston as to yield, if not the whole, a portion of it when urged with a fierce heat. Yet the phlogistians themselves could never obtain from metals what they so earnestly contend for, without the

presence of water. Indeed, Dr. Priestley acknowledges that metals will not give a particle of air without water. As to a metallic basis, they have not yet been able to produce it. Therefore it is obvious, that the contention or difference between the phlogistians and antiphlogistians is this: the former are led away by imagination, and the latter confine themselves to the evidence of their senses. I charged four drachms of iron filings, which I carefully prepared, into a small glass retort; and though I applied heat sufficient to melt the glass, I obtained little more than one cubic inch of inflammable air; and this was produced in the beginning of the process; so that it must have proceeded from moisture. I exposed lead, tin, zinc, bismuth, cobalt, copper, and regulus of antimony, to heat sufficient to melt cast iron, in a well closed deep crucible; and although I sublimed and dissipated all of them (copper excepted), I could not effect the smallest change in their constitution; for what sublimed and adhered to the upper part of the crucibles, possessed its natural brilliancy and specific gravity. Mr. Kirwan supposes that

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fixable air is only formed during calcination in a low heat, but that water is formed in a higher degree. If it were so, red lead would not yield dephlogisticated air; for the phlogistians will not allow the decomposition of water. Mr. Kirwan attempts to obviate this, by saying, that red lead is prepared in a low degree of heat, but that litharge, which requires a higher, will afford none. However, I converted litharge into red lead in a degree of heat not much short of that which will convert red lead into litharge; and it gave dephlogisticated air in small quantities; and by the addition of oil of vitriol I obtained dephlogisticated air from it in abundance, but not a particle of fixable air. Part of the same red lead, exposed to the atmosphere for a few weeks, yielded fixable air both with and without vitriolic acid; which induces me to think that fixable air is not a necessary ingredient in red lead, but that it absorbs it after it is formed.

The truth is, minium contains more dephlogisticated air than litharge does; and, in its transition from the former to the latter, it parts with it, as Dr. Priestley has shewn.



And as litharge contains less of dephlogisticated air than minium, it is the more tenacious of it, and will not give it up until something else is presented to it which has greater affinity to the air than the lead has. Dr. Higgins has shewn, that 7581,5 gr. of litharge, when completely reduced, will yield 6835,2 gr. of pure lead, and that 7680 gr. of red lead will yield but the same quantity; whence he justly inferred, that 6835,2 gr. of lead require, in order to become minium, 98,5 gr. more of air than is necessary to its conversion into litharge. To confirm this, he converted the above quantity of minium into litharge, and obtained during the process 98,5 gr. of air, 24 of which he found to be fixable air, and 74,5 dephlogisticated mixed with phlogisticated air\*. This does not correspond with Mr. Kirwan's account of a similar process; for he found that minium, during its transition to litharge, absorbed air†.

The expulsion of fixable air from minium and other metallic calces, which Mr. Kirwan seems to lay great stress upon, does

\* Exp. and Obs. on Acet. Acid, &c. p. 210.

† Essay on Phlogiston, p. 111.

not in my opinion favour his hypothesis in the least ; for, if the dephlogisticated air absorbed, formed fixable air by an union to the phlogiston of the metal, considering that some metals are revived again without the addition of foreign phlogiston ; it should seem that metals never suffer any part of their natural portion of phlogiston to be carried off: and, indeed, if metals contain what they call phlogiston, it must be so ; for I found that red precipitate, or turbith mineral, recently prepared, afforded no fixable air, although Dr. Priestley discovered a trifling portion of it in dephlogisticated air obtained from mercurius calcinatus. But much depends upon the time they are kept ; for they absorb fixable air from the atmosphere, like all other spongy or porous substances. Hence I think, that the fixable air obtained as well during the calcination of metals, as afterwards from their calces, depends upon some impregnation in the materials, and does not in the least tend to prove the existence of phlogiston in metals. Iron quickly calcined by fire, or in the nitrous acid, will not yield a particle of fixable air, though rust of iron will afford it in

abundance. Mr. Kirwan may object to the former process, by saying, that water is formed during the calcination; but this cannot be said when the calx is prepared by nitrous acid. Therefore, if the calcination in the nitrous acid depended upon an union to fixable air, why should not this afford fixable air as well as the rust of iron, when both appear equally well calcined?

Dr. Priestley calcined iron shavings over mercury in dephlogisticated air, by means of a burning lens, and found some fixed air in the residuum, but it was not more than the 13th of a measure, after the absorption of 7 ounce measures of dephlogisticated air. The same philosopher reduced a quantity of the calx of iron, carefully prepared, by means of spirit, of nitre in light inflammable air; but it does not appear that he obtained fixable air\*. He likewise reduced 17 gr. of lead in alkaline air: the residuum was phlogisticated air, and it did not contain a particle of fixable air. Dr. Priestley reduced 150 ounce measures of light inflammable air to 10 ounce measures, by re-

\* Vol. VI. p. 16.



ducing in it the calx of lead over mercury, and the residuum contained no fixable air \*.

If the fixable air generated during the calcination of the iron, in the above experiment, proceeded from its phlogiston and dephlogisticated air, why was not fixable air formed during the reduction of the calces, whereas they were exposed only to the same degree of heat?

In my opinion, metals contain something not at all necessary to their constitution, which forms fixable air with dephlogisticated air. The phlogisticians must all allow, if metals contain phlogiston or inflammable air, that it is of the explosive kind; for no other is obtained during their calcination in the humid way, whatever menstruum is used. Then why does not this form fixable air with the dephlogisticated air during the revival of the calx of mercury in it, if a substance of the same sort be united to it in the state of fixable air in the calx? The phlogisticians will say, that the heat necessary to the reduction is too great for the formation of fixable air. But then, if so, why will inflammable air from foliated tartar, or from charcoal, which

\* Vol. VI. p. 9.

are known not to contain a particle of ready formed fixable air, generate this under the same circumstance? Or why will it form fixable air in the most intense degree of heat? I ask, if there ever has been an instance of the formation of fixable air by an union of light inflammable air and dephlogisticated air? It appears to me a matter of impossibility. Therefore, how can we suppose that the fixable air produced when we use iron filings and red precipitate, results from an union of both these airs?

Dr. Priestley obtained 40 ounce measures of fixable air from one ounce of red precipitate and two ounces of iron filings\*. From 300 grains of iron newly filed, and 240 of red precipitate, Mr. Kirwan obtained no air; but, on the contrary, there was an absorption. When he used precipitate *per se*, instead of red precipitate, and varied the proportion, and sprinkled the ingredients with water, he got 4,5 cubic inches of fixable air, and 36 of a mixture of dephlogisticated and inflammable air. Mr. De la Metherie obtained no air from equal

\* Vol. VI. p. 27.

parts of red precipitate and iron filings; and from two ounces of red precipitate, and one drachm of iron filings, he obtained a very small quantity of fixable air\*. Equal parts of lead and red precipitate gave no air at all to Mr. Kirwan, though the lead was nearly calcined. 240 gr. of bismuth, and the same quantity of red precipitate, distilled with a low heat, afforded Mr. Kirwan two ounces of fixable air. The same mixture, urged with a strong heat, gave but one cubic inch of fixable air, and the bismuth was calcined. Equal parts of red precipitate and zinc did not produce any air; nor did 200 gr. of copper, and 240 of red precipitate, though the mercury was revived†.

One ounce of red precipitate, and one ounce and a half of iron filings newly made, distilled in a small coated glass retort, afforded but six ounce measures of fixable air, and about one ounce measure of phlogisticated air, though the mercury was nearly revived, and the iron a good deal calcined. I suspect that the iron was impure, for the air had the smell of volatile vitriolic acid

\* 27. Roz. 146.

† Essay on Phlogiston, p. 114, 115.



towards the end of the process; and as I was obliged to receive the airs in water, a small portion might have been absorbed. However, these experiments differ widely from Dr. Priestley's, and clearly prove, that fixable air is not a necessary production in them; but that it depends upon chance, and the presence of some foreign substance which we are not aware of.

Dr. Priestley partially calcined lead in mercury by repeated agitation, with free access of air; and after separating the fluid mercury from a black powder thus obtained, it afforded some fixable air. From six ounces of this black powder he obtained four and a half ounce measures of air, one and a half of which was fixable air\*. 10 ounces of the same powder gave 23 ounce measures of air; 8 or 9 ounces of which were fixable air. 4 ounces of this black powder, and 2 ounces of iron filings, gave only 4 ounce measures of fixable air†. 20 ounces of this, and one of iron filings, afforded but 4 or 5 ounce measures of fixed air‡. 2 ounces of this black powder, moistened and dried again, gave very little fixed air§. Al-

\* Vol. VI. page 258.

† Ib. p. 261.

‡ Ib. p. 262.

§ Ib. p. 265.

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though 4 ounces, treated in the same manner, afforded 120 ounce measures of air, 12 measures of which were fixed air.

Thus we find how these experiments vary in their results ; which shews that the fixable air proceeds partly from some impurities in the materials, but chiefly from absorption of fixable air from the atmosphere. I distilled some mercury with iron filings, in order to obtain it pure, and introduced six ounces of it, and some lead filings, into a five ounce phial with a ground stopple, and tied a bladder half full of dephlogisticated air, which I previously washed in lime liquor, to the neck of it. The bladder being flaccid, I could take out the glass stopple at pleasure, and let in dephlogisticated air when I thought necessary. Having by repeated concussions produced some of this black powder, though the air in the bladder did not seem much diminished, I discontinued the process, fearing that the wet bladder might be a source of fixable air. When I separated the running mercury from it, it weighed near half an ounce, which I quickly introduced into a small coated glass retort, and obtained

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from it one ounce measure of air, which, although it rendered lime-water a little turbid, was not sensibly diminished, and a candle burned in it somewhat better than in common air.

Having enumerated those experiments which the phlogistians adduce as the chief support of their doctrine, I think, they do not in the least help to prove the existence of phlogiston in metals. Let us review them all, and carefully compare their different products of fixable air, and we shall be convinced that it cannot result from any necessary principle in metals; for, if so, the products should be invariably the same under the same circumstances.

Besides, I think, the reduction of one metal by another, in the dry way, rather proves that they contain no such thing as the matter of light inflammable air, or phlogiston. For, let us suppose the dephlogistified air to be united to the phlogiston of the metal, in the state either of fixable air or water, and these to be attached to the metallic basis with any force; is it likely that the phlogiston of another metal, which is intimately combined with its own basis, should disturb  
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this union in the least? The phlogistians may say, that the basis of the reviving metal (we will take, for instance, copper) attracts the fixable air or water of the calx at the same time that the basis of the calx attracts its phlogiston; and so, by a double affinity, effect a decomposition. But I would observe, if such a decomposition should take place, in consequence of the influence of their different metallic bases, that it must be impossible for us to obtain either water or fixable air, as a product resulting from any of the constituent principles of the metal, in the degree of heat necessary to reduce red precipitate. Because, if the iron, or copper, or zinc, or bismuth, all of which will reduce a mercurial calx, should exchange their phlogiston for the fixable air or water of the calx, they must undoubtedly retain this with at least as much force as they do their phlogiston; and it is well known that no heat will expel this from them.

## SECTION

## SECTION VII.

*Of the Calcination of Metals by Steam, and  
the Decomposition of Water.*

**M**R. Lavoisier has shewn us, that steam, when brought in contact with red hot iron, calcines it, at the same time that inflammable air is abundantly produced; from which he inferred, that the water is decomposed. He likewise found that the water is decomposed by iron without the assistance of heat; for he obtained inflammable air by confining iron filings and water over mercury. Dr. Priestley, who has made a vast number of very accurate experiments on the same subject, has found that 294 gr. added to the weight of a quantity of iron, made it to yield 1000 ounce measures of inflammable air, which he estimates would weigh 60 gr. and which is nearly 5 to 1\*. But this estimation, ac-

\* Vol. VI. p. 121.

cording to Lavoisier and Kirwan, is too high. Dr. Priestley likewise found, that the addition of 12 ounce measures of dephlogisticated air added 6 gr. to the weight of the iron which had been fused in it. Therefore, the dephlogisticated air absorbed, carries with it into the calx the quantity of water it holds in solution. Whether a quantity of dephlogisticated air, when as much water as possible is abstracted from it, would calcine the same weight of iron, or any other metal, that it would in its ordinary state, is very well worth ascertaining. As this cannot be done without the assistance of a lens, it is not in my power, at present, to make the experiment. The same philosopher observes, that, making an allowance for the small quantity of dephlogisticated air expended in the formation of fixable air during calcination, which did not exceed the 13th of an ounce measure in 7 ounce measures of dephlogisticated air, the quantity of water produced by the reduction of the iron in light inflammable air, nearly corresponded with the weight of both airs. He moreover observes, that the loss of weight in the iron, after its reduction,

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tion, was equal to that of such a quantity of dephlogisticated air as would have been one half of the bulk of the inflammable air that disappeared in the process \*. A mixture of 1 part of dephlogisticated air and 2 of light inflammable air, provided the airs be pure, will, by passing the electric spark in it, form water, as Mr. Cavendish has shewn; which proportion very well agrees with the above estimation of Dr. Priestley. All these facts strongly concur in favour of the decomposition of water. I charged half an ounce of charcoal into a small tubulated retort; the orifice was very small, and well fitted with a stopple, though, from its conical figure, it was readily taken out at pleasure. Having then exposed the charcoal to a strong heat until nothing came over but pure inflammable air, and this very slowly, I took out the stopple, and poured in nearly half a thimble full of water, and instantly closed it again; when 3 or 4 ounce measures of air gushed from the retort with violence, and then ceased giving out any more until fresh water was

\* Vol. VI. p. 121.

introduced.

introduced. Thus I obtained 10 or 12 cubic inches of air, of which one-fifth was fixable air, and the remainder inflammable, intermediate, I thought, between the light and heavy.

It is very well known that charcoal is wholly convertible into inflammable air, and that this inflammable air cannot, by any means whatever, form fixable air without the presence of dephlogisticated air\*. Therefore water must have been decomposed in the above experiment, by which the matter of charcoal was supplied with dephlogisticated air. Dr. Priestley converted the whole of a quantity of charcoal into inflammable air, without the slightest appearance of fixable air†.

\* It may be supposed that the atmospheric air, by pressing into the retort, contributed to the formation of the fixable air; but if so, fixable air would have been produced by merely taking out the stopple, which was not the case: besides, atmospheric air could not rush in during the short time the stopple had been out, considering that the charcoal yielded inflammable air, and that the pressure of the water up the neck of the retort must more than counterbalance the external pressure of the atmosphere.

† Vol. VI. p. 245.

Mr. Lavoisier, having carefully calcined a quantity of charcoal, in order to expel any water or fixable air it might contain, introduced 248,62 gr. troy of it into an iron tube lined with copper, and having passed through it 1122 gr. of water, in the state of steam, obtained 6644 cubic inches of air, whose weight he estimated at 550 gr. one-fourth of the bulk of which he found, by introducing caustic alkali, to be fixed air; and there remained 5 grains of ashes in the tube. As the weight of the airs produced was more than double that of the charcoal, he inferred that the water must have been decomposed; its oxygenous principle uniting to a portion of the charcoal, and forming fixable air, while the remainder acquired an aerial state, and mixed with the inflammable air of the water. That water had been decomposed in this experiment is evident; else, whence came the fixable air? for, from Mr. Lavoisier's previous treatment of the charcoal, it could not contain any.

Mr. Kirwan does not allow the decomposition of water in the above experiment. He supposes that the fixable air came from the

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the charcoal, being one of its constituent principles, and that the inflammable air is its other constituent principle, and that the additional weight proceeded from the solution of water in both airs.

Mr. Kirwan's first supposition is absolutely contradicted by Dr. Priestley's experiments\*, where he has shewn that charcoal does not contain an atom of fixable air. Therefore, to say any more on the subject would be superfluous. That water is held in solution in all airs, is what we do not dispute, but not in that quantity which the phlogistians imagine. A small quantity of moisture is undoubtedly necessary to the conversion of charcoal into pure inflammable air: if a little more be used, fixable air is produced in very small quantities; but if a larger portion of water be used, the quantity of fixable air is still greater. The extremes Dr. Priestley observed in the proportion of fixed to the inflammable air has been from one-twelfth to one-fifth of the whole. Why the small quantity of water necessary to the aerial state of charcoal should not be decomposed, is difficult to be ac-

\* Vol. VI. p. 345.

counted for, especially when a larger quantity is readily decomposed. I exposed some wort to dephlogisticated air until it began to ferment, yet the air was not in the least diminished, though the liquor acquired an acid taste. The same change took place in the liquor when I prevented all communications with dephlogisticated air.

These facts narrowly inquired into, will remove all doubts respecting the decomposition of water. If it were not decomposed, we could not account for several facts relating as well to the calcination, as the reduction of metals. Let us even suppose the inflammable air to come from the metal in consequence of a superior attraction of its basis to water; is it likely that this would dislodge the water again in any degree of heat, especially when the inflammable air is combined with fire? It may be said, that intense heat dissolves the union of the water and the metallic basis. But should not, as already observed, the same cause prevent the union of the inflammable air to the metallic basis, if it even were as fixed as water, and uncombined with fire, unless we suppose phlogiston to have greater attraction

attraction to the metallic basis than water has? Then, water could never expel inflammable air from the metal.

To account for the calcination of metals by steam, &c. and for the reduction of these again to their metallic splendour in inflammable air, we must, in my opinion, have recourse to a mode of reasoning quite different from the preceding; and consider metals to be simple bodies, whose ultimate particles attract dephlogisticated air with greater force than light inflammable air. The phlogistians may say, that light inflammable air in this case could not decompose metallic calces; but this is foreign to that which I urged last against them. For, metals being fixed bodies, and dephlogisticated air having strong attraction to fire; when calces are exposed to heat, the force of union between them is much weakened, as is evident by the reduction of gold, silver, and mercury by heat alone, having less attraction to dephlogisticated air than the other metals.

To render this more intelligible, let us suppose dephlogisticated air to be attached to the metal in a common temperature,



perature, with the force of 7, and the attraction of light inflammable air to dephlogisticated air to be any degree below this, we will say the force of 6. Let us now suppose this compound or calx to be exposed to intense heat, though not strong enough to decompose it, yet sufficient to reduce its force of union to its dephlogisticated air to  $5\frac{1}{2}$ . If inflammable air were brought in contact with the calx in this state, is it not reasonable to suppose that it would deprive it of its dephlogisticated air? But then I ask the phlogistians, whether the inflammable air could unite to the metal under these circumstances?

I think this alone, strictly considered, would go a great way towards overthrowing the phlogistic theory.

## SECTION VIII.

*Of the Reduction of Metallic Calces by means of Charcoal, and the Formation of Fixed Air.*

**D**R. Priestley has observed, that fixable air must have been actually formed during the union of heavy inflammable air and dephlogisticated air, as he often found that the fixable air produced, exceeded the weight of the inflammable air.

Dr. Higgins has shewn (and I think I am authorized to particularize it, for I had an active share in all the experiments set down in his last publication), that 3,15 gr. of the purest dephlogisticated air, and 1,1 gr. of inflammable air from foliated tartar, afford, when inflamed by the electric spark, 2,85 gr. of fixable air. As the weight of the fixable air fell short of that of the two airs employed, by 1,4 gr. and as there had been a quantity of moisture precipitated, Dr. Higgins supposes that a part of the dephlogisticated

phlogisticated air unites to phlogiston, and forms water, while the remainder, which he estimates to be two thirds of the whole, unites to the acid matter of acetous acid, as he is pleased to call it, and forms the fixable air. When he used inflammable air from charcoal, the result was the same. These experiments clearly shew, that fixable air is composed of the matter of charcoal and dephlogisticated air. I have my doubts respecting the water produced in the above experiment: in my opinion, the most part of it is precipitated from both airs on their contracting an union, as the compound cannot hold in solution as much water as its constituent principles in their simple aerial state; although heavy inflammable air from foliated tartar contains light inflammable air, as appears from Dr. Austin's experiments. But this I consider to be as foreign to the gravitating matter of charcoal, as the matter of sulphur is to the inflammable air, which holds it in solution in the state of hepatic gas. For both will burn, or, in other words, will unite to dephlogisticated air, and form separate compounds. I think, neglecting to discriminate

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nate between the light and heavy inflammable airs, has been the chief cause of all the errors and confusion that at present prevail in the science of chemistry.

Dr. Higgins introduced some pieces of well burned charcoal into a deep crucible, and covered them over an inch deep with powdered charcoal. Having luted on a cover, he exposed them for two hours to heat sufficient to melt silver; he then placed the crucible in such a manner, that the powder might remain red hot for some time after the pieces next the bottom had cooled. This he had done in order, as the charcoal must imbibe something on cooling, both to supply it with inflammable air, and to prevent a communication with the external air, which the charcoal would have otherwise imbibed.

One hundred and twenty grains of this charcoal quickly powdered were well mixed with 7680 gr. of litharge, which had been previously fused to separate any uncalcined lead which it may contain. This mixture was charged into a coated retort just large enough to contain it, so that the common air must have been nearly secluded. Being then

then placed in a reverberating furnace, and heat duly applied, it yielded by estimation, after cooling to the mean temperature of the atmosphere, 384 gr. of fixable air, at the rate of ,57 gr. to a cubic inch, 8,704 of phlogisticated air, and 0,911 gr. of dephlogisticated air, besides 49 gr. of water. On breaking the retort, 3888 gr. of revived lead were found, besides some vitrified litharge; but not an atom of charcoal was left, nor was there a particle of inflammable air produced\*. Now let my reader consider the weight that 3888 gr. of lead acquire by its conversion to litharge, and the quantity of inflammable air that 120 gr. of charcoal will afford (which, according to Dr. Priestley, is about 360 ounce measures), and he will find, making an allowance for the phlogisticated air, that these nearly correspond with the proportion of heavy inflammable air and dephlogisticated air necessary to the formation of fixable air by the electric spark. Hence we may conclude, that not a particle of charcoal entered into the constitution of the

\* Exp. and Obs. on Acet. Acid, Sect. XIX. p. 274-276.

revived lead, but must have been wholly converted into fixable air. Mr. Kirwan cannot say, that this quantity of fixable air existed ready formed in the charcoal, when it is more than two thirds the weight of the charcoal; nor can he attribute this weight to water. Then I ask the phlogistians, whence came the dephlogistified air which formed this fixable air? If they can answer this without contradicting themselves, it is more than I at present foresee. For, in the first place, if they should say that the metallic calx affords fixable air, or that its fixable air is decomposed, by which the charcoal is furnished with dephlogistified air, they contradict their own assertion; for they do not allow the refractory calces to contain any such thing, but, on the contrary, they suppose these to be combined with water. In the second place, if they should say that the dephlogistified air is supplied by the water of the calx, it is contradictory to their own principles, for they do not allow the decomposition of water.

## SECTION



## SECTION IX.

*Of the Solubility of Metals.*

**M**ETALS in their simple state are insoluble in water; but when combined with acids they are soluble. Iron and sulphur fused form an insoluble mass; iron and dephlogisticated air form likewise an insoluble compound; but iron, dephlogisticated air, and sulphur will form a very soluble compound. Phlogisticated air in its simple state has no sensible affinity to metals; yet, when combined with dephlogisticated air, it will unite to them and render them soluble. The affinity of the marine basis to metals is not known; but that they have greater attraction to the dephlogisticated air attached to it than they have to the basis itself, has been already demonstrated. That the attraction of the marine basis to metals is increased by their previous union

union to dephlogisticated air, may be inferred from its property of dissolving the calces of those metals which will not yield to it in their simple state. That common marine acid has an attraction to dephlogisticated air, is very well known; and it has been above observed, that, when fully saturated with this, it will not affect metallic calces, though it will dissolve those metals which the common marine acid will not touch. Oils will not dissolve metals in their simple state, provided the oils be pure, except iron and copper, which are destructible wherever they meet moisture and fixable air, both of which are generally present in oils. But the oils will unite to the calces, and constitute soluble saponaceous compounds. As oils have an attraction to dephlogisticated air, though they cannot unite to it in a common temperature, nor take it from the metals but by the assistance of a strong heat; it may so far influence them as to promote their union to metallic calces. It is clear from these facts, although dephlogisticated air alone will not render metals soluble in water, that it is through its mediation,

tion, or influence, that a third body will unite, and form a soluble compound. But which of the three substances has this solvent power most inherent in it, is what we cannot pretend to explain; nor is it necessary towards the establishment of the antiphlogistic theory to know this. It is sufficient for us to prove, that dephlogisticated air is indispensably necessary for the solution of metals in every menstruum, except a few which I shall presently observe. The foregoing principles will account for Mr. Kirwan's first four queries, Section 10. I must confess I do not see the force of those eleven queries of his, nor can I find how they oppose the antiphlogistic theory in the least.

The most rational of his queries are explicable in this doctrine; and of these the most difficult to be accounted for is the solubility of some calces in the nitrous acid, while others are insoluble in it. But we may attribute this in a great measure to their property of uniting to more dephlogisticated air when in solution, than they can retain in their dry, pure, calciform state. Thus the calces of lead are soluble in all the acids



acids. The calces of gold, mercury, and silver are likewise soluble in the nitrous acid on the same principle. The calces of iron, tin, bismuth, cobalt, zinc, antimony; &c. when perfectly calcined, contain more dephlogisticated air, together with the quantity which enters into the constitution of perfect nitrous acid, than is necessary for solution; therefore either must lose a portion of their air before they can unite. I do not dispute but the bases of the different acids have, independent of their dephlogisticated air, different degrees of attraction to the different metals. I have shewn this to be the case in treating of the vitriolic and marine acid.

Mr. Kirwan's 10th query is not easily accounted for: before we can attempt this, we must be acquainted with the constituent principles of fixed alkali. I doubt whether he can give even a plausible explanation of it himself, in his own doctrine. The dissolution of copper in volatile alkali, likewise, cannot be accounted for in any theory until we know more of chemistry. I at one time supposed that it proceeded from the absorption of dephlogisticated air from the

S                      atmosphere;

atmosphere; but I found this not to be the case by experiment. Indeed Mr. Kirwan might as well have asked why liver of sulphur, or mercury, dissolves gold. Mr. Kirwan's last and 11th query has been amply accounted for in describing the effect of metals on vitriolic acid.

## SECTION

## SECTION X.

*Of the Precipitation of Metals by each other.*

**T**HAT some metals attract dephlogisticated air with greater force than others, is now an established fact. Gold, platina, and silver will not unite with it in the strongest heat of our furnaces. Mercury, likewise, will not unite to dephlogisticated air until heated several hundred degrees above that which is necessary for its fusion only. The rest of the metals will absorb dephlogisticated air by mere fusion, but some with greater rapidity than others; as for instance, zinc, bismuth, and arsenic will present the phenomenon of combustion, when sufficiently heated in atmospheric air. Again we find, that those metals which combine with dephlogisticated air with most difficulty, will yield it with the greatest facility. Mercury, gold, silver,



and platina are restored to their metallic brilliancy by mere heat; while all the other calces require the addition of something which has greater affinity to dephlogisticated air than their respective metals, before they can be reduced to their simple state.

The same order takes place in the precipitation of metals by each other in their metallic state. Gold is precipitated in its semi-metallic state by silver, and silver by mercury, and mercury by copper; and all three yield to the rest of the metals. The same law holds good with respect to most of the refractory metals. They precipitate each other according to their different affinities to dephlogisticated air; although there are a few exceptions; but these, I fancy, proceed chiefly from the attachment of the acid basis to the different metals. Thus iron will not precipitate lead from marine acid; and regulus of arsenic precipitates mercury with difficulty from the vitriolic acid. Marine acid will take silver from the nitrous; and as we cannot attribute this to dephlogisticated air alone (both acids having this in their constitution), it is evident, that  
the

the acid bases are differently influenced by the different metals. Indeed, if they had not different forces of attraction as well to the metals as to the alkalies and earths, we could not very well account for the expulsion of one acid by another from these different substances, more especially when the acids are in their perfect state; although we may attribute this very frequently to the agency of fire. Hence we may conclude, though the acid basis disturbs the affinity of the oxygenous principle to metals in a few instances, that we are not from thence to pronounce the invalidity of the antiphlogistic theory.

I have already shewn, in treating of marine acid, that the basis of this acid contributes much to the reduction of the precipitated metal, otherwise the precipitating metal could never deprive it of the whole of its dephlogisticated air; and the same may be said of the other acid bases.

In a neutral mixture of vitriolated copper, the calx is held in solution by volatile vitriolic acid, which is less intimately attached to the copper than its dephlogisticated air.

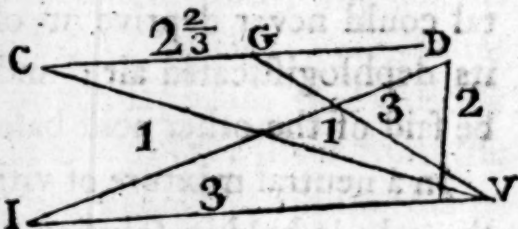
Iron will precipitate the copper from this solution in its simple metallic state.

In order to illustrate this decomposition, I think it necessary to have recourse to the following method:

Let C be copper, D dephlogisticated air, which (let us suppose) attract each other with the force of  $2\frac{2}{3}$ , (to avoid perplexity, reciprocal attraction is not considered) and let this be the calx of copper. Let V, or volatile vitriolic acid, be attached to this compound with the force of 3, and let us suppose 2 of this force to proceed from the dephlogisticated air attached to the copper, and the remainder, which is but 1, to be in consequence of the influence of the copper itself on the sulphur and dephlogisticated air of the volatile vitriolic acid; therefore let G be

the centre of gravity of V.

Let us suppose this to be I



the state of a neutral solution of copper in the vitriolic acid. Here the copper attracts V and D with only the force of  $3\frac{1}{3}$ , and C and D attract V with the force of 3. Let

us



us again suppose I to be iron, which attracts V, or volatile vitriolic acid, with the force of 3, it cannot take it from C and D, which hold it with the force of 3; but it so counteracts the attachment of D and V to C, that it is reduced to  $\frac{2}{3}$ . Let us now suppose I, from its attraction to dephlogisticated air, to influence D with the force of 1: in this case C will be deprived of D and V, for the force of  $3\frac{2}{3}$  must readily obey the power of 4. This, in my opinion, is what takes place in all metallic precipitations. If the precipitant cannot take up the whole of the dephlogisticated air of the precipitated, it is thrown down in a semi-reduced state. Thus lead and silver will precipitate gold of a dirty purple colour, while copper and iron throw it down in its brilliant metallic state. If the iron united first to the volatile vitriolic acid, the resulting compound would not deprive the calx of its dephlogisticated air. For the calx of copper, diffused in a solution of iron in volatile vitriolic acid (although no inflammable air had been disengaged), was not in the least reduced. Hence we may infer, that the whole force of the iron, in order to throw down the

copper in its pure state, must be exerted at once towards V and D; by which, with the assistance of V, V and D move jointly to unite to I, or iron.

If tin be introduced into a neutral solution of tin in the nitrous acid, it is calcined, a calx is thrown down, and dephlogistigated or imperfect nitrous air is produced. Dephlogistigated nitrous air, according to the phlogistians, contains no phlogiston; then I ask, what becomes of the phlogiston of the newly calcined metal? If tin contained phlogiston, either inflammable air or nitrous air would be produced, or a portion of the dissolved tin would be precipitated in its metallic state; neither of which will take place, if the experiment be well conducted. Hence I should suppose, that metals do not precipitate each other in their metallic state, in consequence of a double affinity proceeding from the matter of light inflammable air (or phlogiston), and likewise that metals part with no such thing during their calcination in acids.

Metallic calces do not precipitate each other, as the celebrated Bergman has shewn, but are rather soluble even in neutral solutions

tions of different metals. Hence he inferred, that the same acid takes up the different metallic calces without distinction, provided they have lost a certain portion of their phlogiston; but, to speak in the language of the present time, provided they are not united to too much dephlogisticated air. To ascertain the different degrees of calcination the different metals require to render them equally soluble in the same acid, is a difficult task; for, as the above excellent chemist observed, a very small quantity of dephlogisticated air, over and above a certain portion, will render some metals quite insoluble; and the same may be observed on the contrary extreme.

Hence apparent exceptions arise to this law; for the same acid will take up the some calces, although it will not affect others. Thus the acetous acid readily dissolves the calx of mercury, but scarcely takes up any of the calx of bismuth. However, as the same acid does not make that distinction between the calces that it does between their respective metals, it is evident that dephlogisticated air is the chief cause of metallic solution; although this cannot take place  
when



when the attraction of the acid basis to the metal itself, and to the dephlogisticated air attached to it, is destroyed. For, when the metal is fully saturated with dephlogisticated air, it cannot influence the acid basis to which it must have much less affinity; nor can the dephlogisticated air of the calx influence the acid basis, being already saturated with dephlogisticated air; and the metal, having all its force of attraction to dephlogisticated air expended on the quantity already attached to it, cannot influence the dephlogisticated air of the acid basis in the least: therefore, when perfect calces and perfect acids are mixed, they do not affect each other, except in a few instances, which have been already observed.

Mr. Lavoisier, who first attributed the precipitation of metals in their metallic state by each other, to the superior attraction of the precipitant to dephlogisticated air, deduces the proportion of the oxygenous principle necessary to the solution of different metals, from the quantity of one metal necessary to the precipitation of a given quantity of another metal, by the following

lowing analogy, which, as I cannot at present refer to the author, I shall give in Mr. Kirwan's words: "As the quantity of  
 " the precipitant is to that of the precipitated metal, so is the quantity of the  
 " oxygenous principle necessary for the solution of the precipitated, to that necessary  
 " for the solution of the precipitant. Thus,  
 " since 135 grains of mercury are necessary  
 " for the precipitation of 100 gr. of silver  
 " from the nitrous acid, it is evident that  
 " 135 gr. of mercury require for their solution the same quantity of the oxygenous  
 " principle as 100 grains of silver; and  
 " therefore that the quantity necessary to  
 " dissolve 100 gr. of mercury, is to that  
 " necessary to dissolve 100 gr. of silver, as  
 " 100 to 135. His general formula may  
 " be expressed thus: Let the weight of  
 " the precipitant be  $P$ , that of the precipitated  $p$ , that of the oxygenous principle  
 " necessary for the solution by precipitation  
 " of 100 gr. of the different metals, to be  
 " as expressed in the second column of the  
 " annexed table, and that necessary for solution only, as in the third column."

Metals.

Metals.	Oxygenous Principle.	
	Grains.	For Solution merely.
100 gr. of Platina,	81,690	
Gold,	43,612	
Iron, {	27	
	37	
Copper,	36,000	15, 85
Cobalt,	29,190	
Manganese,	21,176	
Zinc,	19,637	
Nickel,	14,721	
Reg. of Ant.	13,746	22, 383
Tin,	14	23, 555
Regulus of {	11,739	
Arsenic {	24,743	
Silver,	10,800	
Bismuth,	9,622	
Mercury,	8,000	
Lead,	4,470	14, 190

Mr. Kirwan objects to this part of the antiphlogistic doctrine\*, 1st, Because a solution of gold in aqua regia is precipitable in its metallic state, by a fresh made solution of vitriol of iron, but not of copper or any

\* Essay on Phlogiston, p. 131.

other



other metal. The precipitate of gold obtained in the above manner, is generally combined with more or less dephlogisticated air; and considering that 100 gr. of iron fresh dissolved can take 10 grains of dephlogisticated air from 100 grains of gold, that a precipitation should take place is not to be wondered at, especially when gold is rendered insoluble on losing a small portion of the dephlogisticated air necessary for its solution. Besides, the iron does not precipitate an equal quantity of gold, which must make a vast difference. Mr. Kirwan thinks this manner of accounting for it insufficient; 1st, Because a solution of vitriol of copper takes up only 15,85 parts of the oxygenous principle, and yet is capable, by precipitation, of taking up 36 gr. and although it has greater attraction to the oxygenous principle than gold has (according to Mr. Lavoisier), it does not precipitate a particle of gold. 2dly, Because platina is not precipitable by a solution of vitriol of iron, which, in the antiphlogistic doctrine, must retain its dephlogisticated air with very little force, when it cannot take it from  
nitrous

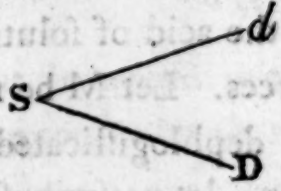
nitrous air, as its insolubility in the nitrous acid indicates.

To the first of these objections I would make answer, that the attraction of copper to dephlogisticated air is not near so strong as that of iron; and its stronger attachment to the acid of solution reduces this still lower, so as to bring both solutions to an equilibrium. To the second cause I would say, that platina, by being soluble in various proportions of dephlogisticated air, may afford the martial solution a portion of it, and still remain in solution.

As copper is precipitated by iron, and likewise as copper is insoluble in diluted vitriolic acid, Mr. Kirwan supposes that the dissolution of copper in a diluted solution of vitriol of iron, by exposure to air or in a boiling heat, is difficult to be accounted for in the antiphlogistic theory; and on this he grounds his second objection. In my opinion, it is very unfavourable to the phlogistic doctrine; because the copper is dissolved, and no inflammable air produced, and yet the iron is thrown down in a calceiform state.

Mr.

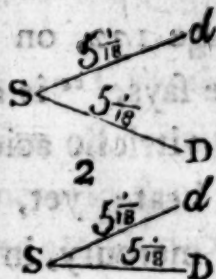
Mr. Kirwan grounds his third objection, page 132, on the following fact: "Iron," he says, "is dissolved by the concentrated vitriolic acid only by the assistance of heat; yet, if to a solution of silver or mercury, in that concentrated acid, a piece of iron be inserted, the silver or mercury will immediately be precipitated in their metallic form, and the iron dissolved. This seems inexplicable in the new theory; for since iron cannot without the assistance of heat deprive sulphur of its oxygenous principle, how does it happen that, without that assistance, it deprives silver or mercury of that principle, though they have a stronger attraction to it than sulphur has?" This, certainly, is a very fair query, and deserves attention. Therefore, I shall give my opinion of it in as clear a manner as I can.

Let the two diagrams,  be molecules of concentrated vitriolic acid; which let us suppose influence each other with the force of 2, which in addition to  $5\frac{1}{11}$  makes  $7\frac{1}{11}$ .

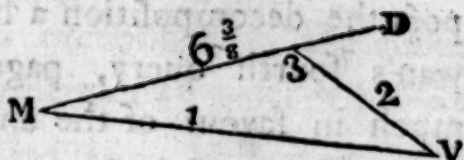
Now,



Now, if iron be introduced into this acid, it will not be dissolved in it; for the force of 7, with which we have already supposed iron to attract dephlogisticated air, being inferior to  $7\frac{1}{2}$ , a perfect neutrality prevails until the force of 2, which we may call the aggregate influence, is diminished; and this is done by fire or water. Again, let us suppose mercury to attract dephlogisticated air with the force of  $6\frac{1}{2}$ ; in this state concentrated vitriolic acid will not influence it, until its aggregate attraction is wholly removed by fire, and then it will readily dissolve it. Let us now suppose the mercury in a state of solution, to be influenced by its dephlogisticated air and volatile vitriolic acid, which is the acid of solution, with the following forces. Let M be mercury, D the quantity of dephlogisticated air necessary for solution; let us suppose these, if there had not been any thing else present to influence either, to attract each other with the force of  $6\frac{1}{2}$ , and

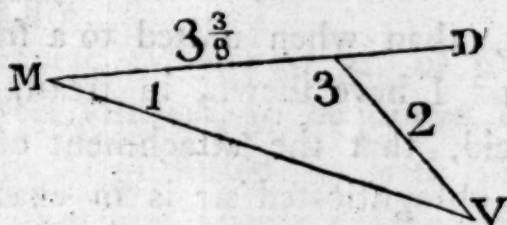


and let us suppose this to be the utmost sum of their reci-



procal attractions. Let us likewise suppose V, or volatile vitriolic acid, to be attached to M—D, or the calx of mercury, with the force of 3; let 1 of this proceed from the mercury itself, and the other 2 from the dephlogisticated air attached to it, which must reduce the attraction of M for D to  $3\frac{3}{8}$ ; which, in addition to the force of 1, that prevails in consequence of the attachment of M and V, makes  $4\frac{3}{8}$ : thus, V and D are attached to M with the force of  $4\frac{3}{8}$ . Now,

if iron were introduced into such a mixture, is



it not to be expected that it would with the force of 7 readily overcome the above force, and precipitate the silver or mercury, even in the presence of concentrated vitriolic acid, which is always inseparable from these solutions, and which, from its weak attachment to the mercurial salt, may op-

T

pose

pose the decomposition a little? Mr. Kirwan's fourth query, page 133, is very much in favour of the antiphlogistic doctrine: for, as I had an occasion to observe above, the precipitation of one metal by another in its calciform state, without the production of inflammable air, at the same time that the precipitant is held in solution, tends strongly to prove the non-existence of the matter of light inflammable air in metals; besides, it is very explicable in the antiphlogistic doctrine. I have already endeavoured to shew upon what principle the acid bases retain their dephlogisticated air with less force, when fully saturated with it, than when united to a small portion; and I have shewn, in treating of nitrous acid, that the attachment of its basis to dephlogisticated air is in exact proportion to the quantity united to it. The same law holds good in all other combinations, and is explicable on the same principles. Almost all bodies will unite with the different substances to which they have an affinity, in various proportions, until they arrive at the point of saturation, which limits their power of chemical attraction.

There



There are a few exceptions to the above law; for, the principles of water will only unite in one proportion, so that we can never obtain it in an intermediate state. The cause of this I have already attempted to demonstrate. I have my doubts whether the same may not be said of the aerial acid. Thus, metals will unite with dephlogisticated air in various proportions, until saturated. If 100 grains of a metal are capable of uniting to 15 gr. of dephlogisticated air only, they will attract and retain 5 gr. of dephlogisticated air with greater force than they will 10 gr. and 10 gr. with greater force than 15 gr.

Let us suppose every 100 gr. of tin, when in perfect solution, to be united to 15 gr. of dephlogisticated air with the force of  $5\frac{1}{2}$ . Let iron attract dephlogisticated air with the force of 7, and let us suppose this force to be reduced to 6, by the accession of  $7\frac{1}{2}$  gr. of dephlogisticated air, and the attraction of the tin to its dephlogisticated air to be increased by losing  $7\frac{1}{2}$  of dephlogisticated air: in this case, iron cannot precipitate tin in its metallic state, although it may have greater attraction to

dephlogisticated air than the tin has. Hence it is evident, that a metal, in order to precipitate another in its metallic state, must not only unite to dephlogisticated air in greater quantities, and attract it more forcibly, but that this superiority of force must be very great indeed.

Mr. Kirwan's fifth, sixth, and seventh queries have been explained, pages 260—1. One ounce of the nitrated calx of mercury, two ounces of Prussian blue, and twenty-four of water, boiled for a few minutes with constant agitation, acquire a cineritious yellow colour. The mercury unites to the tinging acid of the Prussian blue, and forms a soluble salt. If to the filtered solution a small quantity of iron filings and vitriolic acid be added, the whole mass turns black, and the mercury is reduced\*. As iron filings and vitriolic acid produce inflammable air, and as the Prussian acid is disengaged and the mercury revived, Mr. Kirwan supposes, that a portion of the inflammable air unites to the mercury, revives it, and expels from it the Prussian acid.

\* Scheel, p. 162, French translation.

This being urged against the antiphlogistians by Mr. Kirwan, as unanswerable in their doctrine \*, I shall endeavour to inquire into it minutely.

In the first place we are to consider, that the Prussian acid, being united to the calx in its perfect state, cannot take any thing from it during its separation; therefore the reduction must solely depend upon the attraction of the mercury to inflammable air. 2dly, Be it remembered, that Mr. Kirwan considers the calx of mercury as a compound of fixable air and the basis of mercury. Now, I should like to know how the inflammable air can act in this case; for it has two powers to encounter. First, The attachment of the aerial acid to the metallic basis. 2dly, The attraction of the Prussian acid to both, besides its own attraction for fire, which is very considerable. I must confess, as the decomposition depends upon a single elective attraction, I cannot conceive how the inflammable air can expel both acids. If the inflammable air disengaged by the acid and iron filings, should

\* Essay on Phlogiston, p. 123.



unite to the metallic basis, its own proper phlogiston would be disengaged, united to dephlogisticated air in the state of fixable air; for it cannot be said that there is heat sufficient to form water. Then what becomes of the fixable air? for I repeated the experiment with the utmost caution, and could not obtain a particle of fixable air. It cannot be said, that the inflammable air united to the dephlogisticated air of the calx, and formed water, if we suppose it to be already attached to the matter of light inflammable air in the calx; for bodies of the same sort cannot disturb each other's affinity to different substances so materially, as to cause a decomposition.

Let us now inquire into the above process in the antiphlogistic doctrine. I have already shewn, that bodies which have less attraction to dephlogisticated air than sulphur has, may wholly decompose the vitriolic acid, from the nature of its constitution. Thus mercury will calcine in concentrated vitriolic acid by the assistance of heat only, and volatile sulphureous acid is disengaged. The rationale of the production of this acid has been given before. As water has no effect

effect on mercury, it is evident that light inflammable air attracts dephlogisticated air with greater force than mercury does.

If sulphur and the calx of mercury be distilled, volatile vitriolic acid is formed, and the mercury is partly revived; and if a large portion of sulphur be used, cinnabar is formed. Hence it appears, that sulphur has greater attraction to dephlogisticated air than mercury has. These facts kept in view, we can readily account for the reduction of mercury, when vitriolic acid and iron are introduced into the solution of the mercurial calx in the Prussian acid. Iron, as I have already endeavoured to explain, during its dissolution in vitriolic acid, totally deprives the sulphur of its dephlogisticated air; the sulphur again, while in its ultimate division, and before it is influenced by fire, or by the aggregate attraction, recovers this from the water, by which inflammable air is produced. If the calx of mercury reduced into its ultimate division, in which state it must be when held in solution, were in contact with vitriolic acid thus decomposed, is it not reasonable to suppose, that it would

yield its dephlogisticated air to the sulphur, more especially when it retains it with less force than water does? But as water is present, a portion of it is likewise decomposed, by which we obtain inflammable air. Whether the inflammable air itself, at the instant that it is deprived of its dephlogisticated air, may not contribute to the reduction of the mercury, by uniting to its dephlogisticated air, and reproducing water, is what I cannot pretend to determine; although, from the attraction of the matter of light inflammable air to fire, together with the interference of the Prussian acid, I am rather inclined to suppose it does not. The mercury being thus deprived of its dephlogisticated air by the superior attraction of sulphur to that principle, rejects the Prussian acid, as having no sensible attraction to it in its metallic state.

NOTE.



## N O T E.

**F**INDING that Mr. Berthollette, in his notes to the French version of Mr. Kirwan's Essay on Phlogiston (which I had not seen until my section on marine acid had been printed, which is now some months since, the press has been so very tedious), affirms, that dephlogisticated marine air is not decomposed by inflammable air, as Mr. Kirwan has asserted, I made the following experiment :

I poured some colourless nitrous acid highly diluted upon a quantity of manganese, in order to separate any calcareous earth it might contain (the perfect acid having no effect on the pure calx of manganese), and triturated them for some time; then filtered the solution, and washed the calx repeatedly with hot distilled water, until the whole of the nitrous acid was washed away. Having introduced it into a retort, I poured some pure marine acid upon it; and, when it had worked some time, received some of the air in hot distilled water :

ter : equal parts of this and inflammable air produced from vitriolic acid, which stood in lime liquor for two days, were mixed over lime water; the marine air was gradually absorbed, no precipitation took place, and the inflammable air did not seem diminished. I repeated the experiment with the same result. In hastily perusing the page in which Mr. Kirwan mentions his experiment on inflammable and dephlogisticated marine air over lime water, I supposed, he meant, that no fixable air had been produced during the union of both airs: this was my chiefest motive to repeat the above experiment, the result of which tends to corroborate my arguments on that subject,

*An Analysis of the Human Calculus, with Observations on its Origin, &c.*

INTO a small earthen retort well coated, I introduced one ounce and three quarters (Troy weight), or 840 grains of dry and well powdered calculus, which, on being broke, appeared to be laminated with a small nucleus, which was likewise minutely laminated. It was composed of coats or layers somewhat like an onion; the outward crust appeared very porous, but increased in firmness of texture towards the centre. The retort thus charged was placed in a side furnace, with a conical glass tube, and an air apparatus adjoined to it. The first impression of fire after the air of the vessels was expelled, occasioned a slow emission of an elastic fluid, the first measure of which appeared to consist of equal parts of phlogisticated and fixed air.

The 2d measure  $\frac{2}{3}$  fixable,  $\frac{1}{3}$  phlogisticated.

3d  $\frac{2}{3}$  ditto,  $\frac{1}{3}$  ditto.

4th  $\frac{2}{3}$  ditto,  $\frac{1}{3}$  inflammable.

5th, 6th, and 7th measures same as the last.



last. Here the elastic fluids began to come over very fast, attended with an urinous smell. The 8th measure consisted of  $\frac{2}{3}$  fixable,  $\frac{1}{3}$  inflammable, with an alkaline smell, 9th measure  $\frac{2}{3}$  fixable,  $\frac{1}{3}$  inflammable, and burned with a greenish flame. The elastic fluids now issued so rapidly, it was impossible to keep an exact account of the number of measures; and as I was obliged to work in mercury, the measure which I used was small, containing but five cubic inches; therefore I only examined the elastic fluids at different periods of the process. About the fourteenth measure by conjecture, a very pungent alkaline, urinous and suffocating smell was very sensible, not only on the surface of the mercury, but throughout the laboratory. The sixteenth measure was rapidly attracted by lime water to  $\frac{1}{3}$ , and the lime water was not rendered so turbid as it ought to have been, if all the air absorbed had been fixable air: on continuing the agitation the contraction still went on, though much slower than at first, until the air was reduced to  $\frac{1}{3}$ , which was inflammable; the last portion, that was slowly absorbed, precipitated the lime very fast. After losing  
 7 about

about five measures, the next was rapidly contracted in common pump water partially impregnated with fixable air, until reduced to  $\frac{2}{3}$ , and here seemed stationary, though frequently agitated; but on removing it to lime water, it was contracted  $\frac{1}{6}$ , rendering the lime water turbid. From these facts it appears, that fixed and alkaline airs issued at the same time; but why they did not unite in their passage, or when received into the measure, is a mystery to me; probably the small quantity of inflammable air interfered. From the beginning of the 10th measure, a black charry and greasy matter began to line the conical tube and the air vessel; and may not the alkaline air dissolve this partially, though not in such proportion as to render it solid, yet at the same time to weaken its attraction for fixable air? Were they to stand for some time, I do not doubt but mild volatile alkali would have been formed; but this circumstance did not occur to me during the process. The last proportions continued for four measures, and then the alkaline air increased to  $\frac{1}{4}$ , and the remainder was inflammable. It is remarkable, that this proportion

proportion of alkaline and inflammable airs should burn as well as if the whole had been inflammable. At this period more than two thirds of the process were over, and the proportion of alkaline air decreased, while that of the inflammable air increased, until towards the end, when the last nine measures were all inflammable, and the operation ceased, though the retort was urged with a white heat.

On breaking the retort when cold, I found a black powder on the bottom, which weighed 95 grains; this I digested in ten ounces of distilled water for one hour, and then filtered and evaporated it to two ounces, when a yellowish powder was deposited; and on letting the whole stand for one night, no crystals were formed. I filtered the liquor to separate the powder, and evaporated the filtered solution to one ounce, during which time it continued to deposit more of the same powder; this again I passed through the same filter I used last, in order to have it all upon one filter, and when the liquor was all through, I washed the powder with distilled water, which I added to the rest of the solution. This being evaporated to  
eight



eight pennyweights, or half an ounce, began to deposit a very white powder, and to emit a subacid astringent vapour, not unlike vitriolic acid. The white precipitate when collected, washed, and dried, weighed one grain: it had a shining appearance, and felt very soft, not unlike mica in powder: exposed to a white heat for ten minutes, it acquired no change, but looked rather whiter. It dissolved in distilled water; caustic volatile alkali caused no precipitation; mineral alkali, and the acid of sugar, rendered the solution turbid, and likewise nitrated terra ponderosa: hence I inferred that this powder was selenite. After separating the selenite, I evaporated the remaining part of the solution to dryness, with a gentle heat, during which time it emitted subacid vapours. The powder weighed eleven grains, was of a dirty yellow colour, and had an aluminous taste. To this powder I added as much distilled water as was nearly sufficient to dissolve it; and then put it by for three weeks, being interrupted by some other business. At the expiration of this time, small transparent, and seemingly cubical crystals appeared

on the side of the vessel, above the surface of the solution; and these likewise had an aluminous taste. I dissolved the whole in distilled water, and filtered the solution: acid of sugar had no effect on it at least for five minutes; caustic volatile alkali occasioned an immediate cloudiness; and the solution when filtered, though the caustic alkali predominated, was rendered turbid by a solution of mineral alkali; nitrated terra ponderosa threw down a copious precipitate, and Prussian alkali detected a small portion of iron. This aluminous solution, as I may now venture to call it, left on the filter a yellow substance, which when washed and dried weighed half a grain; it dissolved in nitrous acid without effervescence; acid of sugar caused no precipitation, but caustic volatile alkali threw down a precipitate, which dissolved in distilled water. This solution was rendered turbid by the acid of sugar, and muriated terra ponderosa; but caustic volatile alkali, or lime water, had no effect on it. The solution of selenite in either of the mineral acids, and its precipitation undecomposed by caustic volatile alkali, should always be guarded against by every experimentalist.

The

The yellow powder first deposited during evaporation from the solution (page 286) weighed two grains and a half, and, exposed to a tolerably strong heat, acquired a deep orange colour. I digested it with two ounces of distilled water in a sand heat for half an hour, and then filtered the solution, which did not contain any thing but selenite. A yellow powder was left on the filter, which weighed  $\frac{3}{4}$  of a grain; it seemed to be iron, and such I found it, for marine acid readily dissolved it; phlogisticated alkali precipitated Prussian blue, and tincture of galls turned the solution black; muriated terra ponderosa seemed to detect a vitriolic impregnation; but, on examining the marine acid, it contained a small vestige of vitriolic acid, though not so much as appeared to be present in this martial solution. Indeed the acid vapour rising from the solution of alum, during the deposition of this iron and selenite, renders it probable that it may be partially combined with vitriolic acid, in such a proportion as not to render it soluble in water, and in such a state as to be disengaged by marine acid. Thus separating all that was soluble in distilled water from the charry substance left in the earthen

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retort,



retort, I dried and weighed the remainder, and found the loss of weight by this treatment to be fifteen grains. I calcined the remaining eighty grains in an open crucible exposed to a strong red heat; it was difficult of calcination, and took three quarters of an hour to be reduced to a bright grey powder; it first burned with a flame, and afterwards calcined with very vivid sparks at every fresh surface exposed to the air; when thoroughly calcined and cold, it weighed twenty-one grains, having lost fifty-nine grains during calcination. I plunged it into six ounces of hot distilled water, and when it stood half an hour filtered it: the solution tasted like lime water, turned syrup of violets green, and diluted vitriolic acid had no effect on it; but aerated volatile alkali, and acid of sugar, rendered it turbid. The remaining part of this powder left on the filter, when well dried, weighed sixteen grains; therefore, five grains of lime seem to have been taken up by the distilled water; these sixteen grains dissolved in nitrous acid, first, with a little effervescence, and when this ceased the solution went on very slow, until the whole

whole was taken up: acid of sugar caused no precipitation in this solution, but caustic volatile alkali precipitated the whole; about one grain of Prussian blue was thrown down by the phlogisticated alkali, or perhaps more, for I could not separate it from the filter. I digested the precipitate, when well washed and freed from the volatile alkali, in distilled vinegar, which took up with effervescence one grain and a half, which was precipitated by caustic volatile alkali. I washed what was insoluble in the vinegar, and digested it in distilled water for half an hour, then filtered the solution: caustic volatile alkali had no effect on this solution; but acid of sugar and nitrated terra ponderosa caused an immediate cloudiness. Seven grains and a half of the powder, which was insoluble in distilled water and acetous acid, were readily taken up by diluted vitriolic acid, and precipitated by caustic volatile alkali: so the sixteen grains last treated, seem to contain of clay seven grains and a half; of selenite six grains; of magnesia one and a half; and of iron one grain. The proportions of the different ingredients are as follow, viz.

U 2

Iron

Iron	- - - - -	$2\frac{1}{9}$ Grains
Selenite	- - - - -	11 Ditto
Clay	- - - - -	$7\frac{1}{2}$ Ditto
Alum	- - - - -	8 Ditto
Pure calcareous Earth	-	5 Ditto
Aerated Magnesia	- - -	$1\frac{1}{2}$ Ditto
Charry combustible Substance		59 Ditto

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Total  $94\frac{1}{9}$  Grains

I found a darkish yellow saline sublimate adhering to the neck of the retort, of a lamellar spongy texture, except the inner part next the retort, which was more compact, and coloured: this being carefully collected, weighed 425 grains, and readily dissolved in half a pint of hot distilled water. I filtered the solution, and separated a coally substance, which when washed and dried weighed ten grains, and, when exposed to a red heat, burnt with a greenish flame, and emitted white fumes, in smell not unlike vitriolic ammoniac: the residuum after calcination weighed half a grain, and was of a whitish colour; it seemed insoluble in distilled water, but nitrous acid dissolved it with effervescence; acid of sugar caused a very little precipitation,



tion, which did not take place until it stood some time; but caustic volatile alkali instantly threw down a precipitate, which was taken up, when washed, by acetic acid: The quantity was too small to be examined more accurately, but it seemed to possess the properties of magnesia. The saline solution had the colour of small beer, and, when evaporated to two ounces, did not deposit any thing, nor on cooling yielded any crystals. The black matter which lined the conical tube and air vessel, weighed twenty-eight grains; indeed it adhered so fast to the glass, it was impossible to collect the whole from the broken fragments, so that a few grains may be lost. I dissolved it in distilled water, and separated four grains of a black coal from it, which did not differ in the least from that obtained from the former sublimate: this solution likewise evaporated to one ounce, and, after standing one night, did not shew the smallest appearance of a deposition, or a crystallization. I mixed both solutions together, and evaporated them to one ounce; which, when cold, acquired the consistence and colour of treacle,

cle; so that I was now assured this was not a crySTALLIZABLE salt, and that a sufficient knowledge of it could not be acquired by this treatment. I charged it into a small tubulated glass retort, with six ounces of distilled water, in order to wash it down; and then placed it in a sand bath, and distilled over three ounces of water, which seemed to be impregnated with nothing but a small quantity of the solution, which adhered to the neck of the retort, and which gave it a light straw colour: this being removed, I applied a clean receiver; and when about half an ounce more of the liquor came over, the distillation was attended with an alkaline smell, merely sensible, until an ounce and a half of the liquor passed over; and then it got so very pungent, though the distillation was carried on very slow, and the vessel kept cool, that I was convinced of its being in a caustic state; but a small quantity of mild volatile alkali adhered to the lower part of the neck of the retort, part of which was washed down by the distillation, so that it was in vain for me to attempt to ascertain the proportions which the mild and caustic  
alkali

alkali bore one to another. The volatile alkaline solution in the receiver, had the colour and smell of spirits of hartshorn, but more empyreumatic, and like spirits of hartshorn, when exposed to the air for some time, acquired a deeper colour, in consequence of part of the alkali escaping, and the rest attracting fixable air, which rendered it incapable of keeping the charry matter in solution, which it had before dissolved. When all the liquor had passed over, and nothing appeared in the retort but a small black mass, I raised the fire; and, according as the heat increased, this black substance acquired a white colour, with a kind of arrangement on the surface, which was occasioned by the heat applied to the bottom of the retort being only sufficient to raise the salt to the top of the charge; but when the sand got nearly red hot, white fumes began to appear, which condensed on the upper part of the retort, and a little way down the neck. The process lasted until the charge was nearly red hot, when the white fumes ceased, and nothing else passed over. On breaking the retort the following day, I collected the sublimate, which weighed



seventy-two grains, and a black porous brittle substance was found on the bottom of the retort, which weighed twelve grains; and which, when exposed to a strong red heat, emitted white fumes, with a slight alkaline smell; by this process it was reduced, with very little appearance of combustion, to a grey powder, which weighed three grains: this I cannot give any account of, as it has met with an accident; but I could venture to say, that four grains of the black powder were the same as the sublimate, and that the remaining five grains consisted of volatile alkali, and a charry combustible substance.

Having the sublimate now, as I thought, tolerably pure, and wishing to know its nature and properties (as I suspected it to be a combination of volatile alkali and some acid), I took five grains of well burnt and powdered quicklime, and with it mixed five grains of the sublimate, but without the least smell of volatile alkali; and thrown upon a red hot iron, it emitted white fumes: the same proportion of vegetable alkali and sublimate had the like effect. I made two equal divisions of the remaining

maining part of the sublimate, which was sixty-two grains; the one I mixed with two ounces of distilled water; it readily diffused through it, being in fine powder; and on the other poured sixty grains of vitriolic acid, diluted with half an ounce of distilled water: having thus mixed them in two large beer glasses, I was obliged to set them by for six weeks, being interrupted by other chemical experiments; and at the expiration of that time, neither seemed to be much acted upon. I poured the vitriolic mixture into a small matrafs, and boiled it on sand for half an hour, with two ounces of distilled water, when the whole was taken up: the solution looked clear, and deposited nothing on standing; mild mineral alkali had no effect on it; but mild vegetable alkali threw down a copious precipitate in white floculi, which was redissolved by caustic alkali, lime water, and partially by mild mineral alkali. Phlogificated alkali, acid of sugar, and acid of tartar, had no effect on this solution. The other portion of sublimate, which I mixed with water, was very little dissolved, and

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in pouring it into a matrafs, small round lumps which appeared on the bottom of the glafs, drew my attention; they were fix or feven in number, fome weighing more than one grain, and the fmalleft about half a grain. They were very hard and compact, with a very fmooth furface, and in figure refembling the nucleus found in this calculus. I charged the whole into a matrafs, with three ounces of water, and boiled it on fand for three quarters of an hour, when about one half was taken up; the folution filtered very clear while hot, but on cooling it got turbid, and in time depofited white floculi, which were redif- folved by cauftic volatile alkali and lime water: it turned fyrup of violets green; but this may be occafioned by its retaining volatile alkali, though it had not the fmalleft appearance of fuch impregnation. I have often obferved, that, fometimes, the pureft fixed vegetable alkali contains volatile alkali, notwithstanding the many operations and different degrees of heat it muft undergo before it arrives at that degree of purity in which we find it fold at the fhop,  
under



under the name of salt of tartar\*. I filtered the solution, to separate what it deposited on cooling: mineral alkali had no effect on it; but mild vegetable alkali caused a cloudiness, which was redissolved by mineral alkali and lime water. Prussian alkali had no effect on this solution; the acids of arsenic, of tartar, of sugar, and of borax, had likewise no effect on it; and also the three mineral acids. I was obliged to discontinue my experiments on this sublimate here, having no more of it, and no calculus to obtain it from.

I introduced five pennyweights, or 120 grains, of the same calculus into a small tubulated retort, and on this poured half an ounce of strong nitrous acid, which acted upon it with effervescence. I collected some of the air extricated during solution, and found it to be fixable, with a small quantity of nitrous air. When the effervescence ceased, I added a quarter of an ounce more

\* I have observed that fixed alkali, when first moistened with water, very frequently produced volatile alkali; and as the constituent principles of volatile alkali were not well known when this paper had been written, I supposed it to be ready formed in the fixed alkali.

of nitrous acid, and digested it in hot sand for one hour, during which time it emitted nitrous vapour and nitrous air; but the latter in very small proportion. When the solution was perfected, I poured it into a small matrafs, with the addition of one ounce of distilled water, and boiled it gently, until the superabundant nitrous acid was nearly expelled. The solution was of a deep yellow colour, and appeared turbid; but, on adding five ounces more of water, and digesting it a quarter of an hour longer, it acquired the colour and transparency of what is called dephlogisticated nitrous acid. On cooling it got a little turbid, and in a few days deposited a darkish yellow powder. I filtered the solution to separate this powder, which, when washed and dried, weighed a little more than a quarter of a grain: pure nitrous acid had no effect on it, but marine acid readily dissolved it; in short, it had all the properties of calx of iron. Being again interrupted, I was obliged to lay the solution by for some time; and wishing to know what effect a long exposure to the heat of the sun would have on it, I placed it in a window, in one of the upper rooms of the laboratory at Oxford, where the sun had full

full power over it four hours every day. A little moisture seemed to exhale from it daily, the weather being hot, and the matrafs, which had a short wide neck, being only covered with a piece of bibulous paper to keep out the dust. Thus situated, in the course of a week a few very small crystals appeared to float on the surface, which in time sunk to the bottom, where they adhered together, so as to form a hard concretion, still retaining a crystalline appearance, but being so small and confused, it was impossible to distinguish their figure: this deposition continued for near a month, and then seemed to cease. I filtered the solution to separate the salt; and, to expedite the process, as I thought, evaporated half an ounce of the liquor away, and then set it by in the usual place for a fortnight longer; but no more of these crystals appeared. I digested the salt, which, when washed and dried, weighed three grains, in four ounces of distilled water for two hours, and no part seemed to be taken up. I decanted off three ounces of the water, and added to the remainder six drops of vitriolic acid, which, by help of digestion, seemed to dissolve it slowly; but on the  
addition



addition of half an ounce more of distilled water, the whole was readily taken up. Acid of sugar had no effect on the solution, but lime water rendered it turbid. I precipitated the whole with caustic volatile alkali, and filtered the solution, which likewise threw down the lime from lime water. I washed the precipitate, and poured distilled vinegar upon it, which did not take it up: marine acid dissolved it; phlogisticated alkali had no effect on the solution; and the acid of sugar caused very little turbidness on standing three or four hours. These appearances induced me to suppose, that this salt was phosphorated clay. The solution being now free from iron and phosphorated clay, had a sub-acid taste, and looked clearer, but still retained a yellow cast: acid of sugar had no effect on it; but nitrated terra ponderosa threw down a copious precipitate; as did likewise the caustic volatile alkali. Mild fixed vegetable alkali (which at first surprised me much) caused no precipitation, but, when I considered the solvent power of fixable air on calcareous earth and magnesia, which earths I knew were held in solution in small proportions, and the quantity of fixable air disen-

gaged by the uncombined and combined acids, I could readily account for the above phenomenon. I charged two-thirds of this solution into a small glass retort; and distilled over two ounces of liquor, which seemed tasteless; but had a very agreeable smell, not unlike rose water. When all the liquor passed over, white fumes appeared in the retort, which were soon succeeded by a slow emission of an elastic fluid. I collected some of this fluid, and found that a candle immersed in it burned with an enlarged flame. Nitrous air did not diminish it in the least; it seemed to be that species of air that nitrous ammoniac is convertible into: no more than thirteen or fourteen cubic inches of this air were obtained; and as soon as it ceased to come over, I observed some salt in irregular crystals in the lower part of the neck of the retort. On increasing the heat, a white salt began to sublime, and adhere to the upper part of the retort. I continued the operation until the bottom of the retort was obscurely red hot, and then raised it in the sand. The following day, when I broke the retort, the quantity of sublimate was so trifling, I could collect but very little from  
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the broken glass: however, there was sufficient to convince me, that it was the same with what I obtained in my former analysis. The salt mentioned above, which crystallised in the neck of the retort, was nitrous ammoniac; it inflamed and detonated *per se*, &c. A grey powder was left on the bottom of the retort, which hot distilled water partly dissolved; muriated terra ponderosa, acid of sugar, and vegetable alkali rendered this solution turbid, but caustic volatile alkali had no effect on it. The remaining part of the powder which the distilled water left behind, was readily dissolved with effervescence by marine acid, and precipitated by caustic volatile alkali: that part taken up by the distilled water seems to be selenite, and that dissolved by the marine acid to be magnesia.

This last mode of treating the calculus, was partly to correct my former analysis, but chiefly in consequence of Dr. Beddoe's very judiciously suspecting, that it contained something which might be decomposed by the strong heat I first used (how far this conjecture was right is very evident); therefore I only attended to the proportions of that which evaded my former analysis.

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The phosphoric acid must have been united to volatile alkali in the calculus, previous to its treatment with the nitrous acid, notwithstanding its superior attraction to calcareous earth: the presence of alum shews how enveloped with an oleaginous matter the volatile alkali and pure calcareous earth must have been; therefore it appears, that the calculus was composed of the following different compounds blended together, viz. selenite, alum, microcosmic salt, mild volatile alkali, lime, and caustic volatile alkali combined with oil, so as to form a saponaceous mass, calx of iron, magnesia combined with aerial acid, clay enveloped by a saponaceous and oily matter, and the sublimate already described. Considering this to be the true state of the calculus in the bladder, the small proportions of clay, selenite, magnesia, and iron, which are the most insoluble of the ingredients, the great solubility of microcosmic salt, and alum, and the miscibility of lime, volatile alkali, and oil in water, tend to shew, that the sublimate is the cementing ingredient: indeed, its insolubility in water, and property of forming nuclei out of the body, as above observed, leave no

room to doubt it. The proportion of the other ingredients, and very likely their presence, depend upon chance, volatile alkali and oil excepted ; therefore this sublimate should be the object of our investigation. May not strict researches into the nature of this singular substance throw new light on the original cause of other disorders, as well as that of the calculus, particularly the gout, which hitherto has baffled the skill of our physicians ? The effect of mild mineral alkali on the sublimate, is worthy the attention of those who may have an opportunity of trying its efficacy. Mild mineral alkali may be taken in large doses, and continued for a length of time with impunity to the most delicate constitutions, only observing a few circumstances ; but this alkali in a caustic state must very often be attended with mischievous consequences. Besides, if we consider that it must enter the mass of blood before any part can reach the bladder, and the small portion of the dose taken secreted with the urine ; and, lastly, the action of caustic alkali upon animal substances, we shall be at a loss to know on what principle

caustic

caustic alkalies have been recommended in preference to the mild. Soap itself might as well be prescribed at once ; for soon after caustic alkali is taken, it must be in a saponaceous state. Fixed vegetable alkali should be avoided, and the preference given to the other two alkalies. As it is evident that alkalies have no real action on the stone in the bladder, though their efficacy has been experienced in alleviating the disease when timely administered, their mode of action is only explicable in the following manner : They either prevent the generation of the sublimate in the system, or else keep it in solution in the mass of fluids ; and being in the utmost degree of divisibility, its ultimate particles are capable of passing through the most minute emunctories, by which it is carried off by other secretions as well as by the urinary. Thus the urine not being saturated with this matter, acts as a solvent on the stone ; and as the most soluble parts are first washed away, it in time falls into fragments of irregular surfaces, which, by their friction, irritate and inflame the bladder, as has been observed by several practitioners.



Allowing that the sublimate is the cementing substance in the calculus, and judging from the effects of alkalies upon it, their *modus operandi* in the constitution, it remains now to inquire into the origin of the calculus. The immortal Scheele has found this sublimate in the urine of different persons, and hence inferred, that it was a common secretion; but it still remains to be ascertained, whether there be a greater quantity of it procured from the urine of patients who have the misfortune to labour under this disorder, than in that of those who never felt its pangs. If this latter should not be the case, another path lies open for our researches, which promises most success. May not a deficiency of volatile alkali in the constitution, be the cause of concretions in the bladder, kidneys, &c. or, which must have the same effect, too great a proportion of acid, which, uniting with the alkali, may take up that portion which would have kept the sublimate in solution, until conveyed out of the system by the urinary and other secretions; and may not this be the phosphoric acid? If this latter should be the case, an increase of microcosmic

cosmic salt must be found in the urine ; but if the former, a decrease of the volatile alkali, and no increase of the neutral salt. The small quantity of phosphoric acid found in the calculus, proceeds from the solubility of microcosmic salt. Do not volatile alkali and phosphoric acid constitute a great part of the human frame ? and is there not a process continually carried on to generate these in the system \* ? and is not this process liable

\* It is nearly three years since I first had an opportunity of making some observations on volatile alkali, which confirmed my opinion of its constant generation in the human system, to supply its continual waste ; and likewise enabled me to form a faint idea of its constituent parts. As others have published some experiments and observations, made subsequent to mine, I find it necessary to be more minute in the following recital, than I otherwise would wish. About the latter end of March 1785, I found that nitrous acid poured on tin filings, and immediately mixed with fixed vegetable alkali, generated volatile alkali in great abundance : so singular a fact did not fail of deeply impressing my mind, though at the time I could not account for it. I mentioned this to Dr. Higgins (for the observation was made in his laboratory), but he took little or no notice of it. Thus, unable to awake his attention to so singular a fact, and having no opportunity of making experiments of my own, I was obliged to lay aside all thoughts of it.

About

liable to be retarded or checked by intemperance, &c. which may vary their quantities and proportions? and may not a due proportion of these be necessary to a vigorous and sound constitution? If so, no wonder that

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About a fortnight after, I mentioned the circumstance to Dr. Brocklesby. He told me he was going to meet some philosophical gentlemen at Sir Joseph Banks's, and desired I would generate some alkali for him to exhibit before them: accordingly I did, and had the pleasure of accompanying him thither.

The December following, I chanced to get acquainted with my late worthy friend, Dr. Caulett, to whom I mentioned the fact already related, respecting volatile alkali, and likewise its copious generation from Prussian blue, fixed vegetable alkali, and water. Pleased with what I told him, we agreed to procure the necessary apparatus for making a set of experiments on the subject. At present it is needless to give a detail of our different experiments; though at that time, when volatile alkali was less known, they might have been of some importance: therefore I shall only give an account of the following, which drew our particular attention. Into a glass cylinder made for the purpose, we charged three parts of alkaline air, and to this added one part of dephlogisticated air; we passed the electrical spark repeatedly in it, without apparently effecting the smallest change. When it had received about a hundred strong shocks, a small quantity of moisture appeared on the sides of the glass, and the brass conductors seemed



an increase or deficiency in either or both of these, should be productive of several disorders. I make not the smallest doubt but a series of accurate experiments, made by a sagacious observer on the latter part of this

seemed to be corroded: when we had passed sixty more shocks in it, the quantity of moisture seemed to increase, and acquire a greenish colour, though at this time the column of air suffered no increase or diminution. On examining the air, it burned with a languid greenish flame, from which we inferred that the dephlogisticated air was totally condensed; it still retained an alkaline smell, and the alkaline part was not readily absorbed by water. This and another phenomenon observed in the first part of this paper, respecting alkaline and fixable airs issuing at the same time, without forming an union, induce me to suppose, that volatile alkali, like other substances, may be found in an intermediate state, and in proportion as it is deprived of one of its constituent parts, that it attracts fire so much the stronger, which counteracts its attraction to other bodies. Thus nitrous air is a compound of phlogisticated and dephlogisticated airs, requiring a larger proportion of dephlogisticated air to condense and render it combinable with alkalies. I often observed, that fixable air obtained from different substances, was not under the same circumstances always condensed with equal facility\*: hence must arise the impos-

\* Since the above has been written, I have been induced to suppose that fixable air is never found in an intermediate state, as observed in the beginning of this volume.

this subject, would be attended with useful discoveries. If God will grant me health and opportunity, I shall persevere in this task, and wish that others would do the same; for the importance and extent of the subject

sibility of ascertaining the specific gravity of the compound elastic fluids. From Mr. Cavendish's famous discovery of the constituent parts of water, we could readily account for the loss of the dephlogisticated air in this experiment; but the quantity of water produced was more than we could expect from this: therefore water must have been precipitated from the decomposed alkali; for volatile alkali, from its great attraction for water, must keep some in solution, even in its aeriform state. From the above circumstances, it might be expected that a contraction of the column of air should take place; but be it considered, that the union took place gradually, in proportion as the alkali was decomposed, and that in this case the expansion must equal the condensation. Being obliged to set out for Oxford, our experiments were suspended, and, alas! never to be resumed. If a young man of uncommon sagacity, perseverance and industry, and whose philosophical mind was strongly bent towards new investigations, promised to extend science, the premature death of the late Dr. Caulett must be a severe loss to society, as well as a grievous one to those who had the pleasure of his acquaintance. During the spring of the year 1786, I often had an opportunity of mentioning different facts to Dr. AUSTIN, relating to volatile alkali, who at that time was too much engaged to pay attention to the subject. In the latter end of June

subject point out to me, that we shall all find work enough, and that our labours will not be in vain, provided they be attended with diligence.

The above Analysis is an exact copy of what has been read before the Royal Society. I am sorry I have not had an opportunity of prosecuting the subject as I would wish, as I promised two years since, when this paper was written. I have made some

1787, I received a letter from him at Oxford (for he then lived in London), requesting my exact mode of obtaining volatile alkali, as he was engaged in that subject. I mentioned the purport of his letter to Dr. Beddoes, our present lecturer in chemistry at Oxford, who had readily seen into the importance of what I told him, and candidly said, it ought to have been made public a long time ago. On my arriving in London the following August, Dr. Austin gave me an account of a set of experiments which he had made, and which actually proved, that volatile alkali consists of light inflammable and phlogisticated airs, not knowing at that time what Mess. Hausman and Bertholet had done. Without depreciating the merit of these two gentlemen, Dr. Austin has an equal claim to the discovery, laying aside priority; as his experiments are as decisive as theirs. Dr. Priestley made the first step towards our knowledge of volatile alkali. See his Sixth Volume on Air.

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experiments,



experiments, but they are not numerous enough, or of sufficient importance, to afford a satisfactory conclusion; for, in order to this, it would require at least 500 experiments. But I hope shortly to have it in my power, to offer the public something on this subject. That the urinary sublimite is present in tubercles found in the lungs of persons who die of pulmonary consumptions, and likewise in what are vulgarly called chalk stones, is what I have experienced; but in what proportion, or whether in quantities sufficient to cause the concretion, is what I cannot say, for I have had but a few grains of each to examine; nor could I procure any more, notwithstanding a diligent inquiry amongst my friends. I have every reason to suspect, that consumptions and scorbutic complaints very frequently arise from a superabundance of this sublimite in the system; and that it is chiefly the cause of the gout and rheumatism, and solely the cause of the stone in the bladder. I make no doubt but these disorders generally proceed from obstructions; and it is probable that either a precipitation of this sublimite in the system, or  
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else a deficiency of some other secretion, which would hold it in solution until conveyed out of the body, may be the chief cause of those obstructions; and likewise, that different degrees of precipitation may produce different symptoms and different disorders.

That mineral or volatile alkali and bark have been useful in the above disorders, has been affirmed by experienced physicians; and I know an instance myself of mineral alkali and nitrous ammoniac being serviceable in a pulmonary complaint of some standing.

With respect to the stone, when it acquires a certain magnitude, it is absurd to attempt to dissolve it in the bladder, it wastes so very slowly, and during this time the patient must suffer vast pain, particularly when the stone acquires a rugged surface; therefore cutting for it at once is much preferable.

Mineral alkali taken in the beginning of the complaint, and before the stone accumulates, will no doubt check its progress, and may in time change that disposition in the habit. Patients who are cut for the  
stone

stone should, I think, take mineral alkali for some time when the wound is healed, but not before, for fear of bringing on a mortification. These are my opinions, or rather queries, respecting the effects of the above salt or sublimite found in the urine, calculus, &c. on the human constitution; and my sole motive for laying them before the public, is to promote an inquiry into so interesting a subject.

I flatter myself, that at least an attentive perusal of the above experiments may point out the ignorance of those empirics who have too long imposed upon the public with their pretended lithontriptics, and likewise that it may tend in future to check such proceedings.



THE END.



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